TECHNIQUE OF ORGANIC CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

Volume V

ADSORPTION AND CHROMATOGRAPHY

TECHNIQUE OF ORGANIC CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

Volume I: Physical Methods of Organic Chemistry Parts I and II *Second Edition*

Volume II: Catalytic, Photochemical, and Electrolytic Reactions

Volume III: Heating and Cooling; Mixing; Centrifuging; Extraction and Distribution; Dialysis and Electrodialysis; Crystallization and Recrystallization; Filtration; Solvent Removal, Evaporation, and Drying

Volume IV: Distillation

Volume V: Adsorption and Chromatography

Volume VI: Micro and Semimicro Methods

Volume VII: Organic Solvents *Second Edition*

Volume VIII: Investigation of Rate and Mechanism of Reactions

TECHNIQUE OF ORGANIC CHEMISTRY
Volume V

ADSORPTION AND CHROMATOGRAPHY

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TECHNIQUE OF ORGANIC CHEMISTRY

INTRODUCTION

Organic chemistry, from its very beginning, has used specific tools and techniques for the synthesis, isolation, and purification of compounds, and physical methods for the determination of their properties. Much of the success of the organic chemist depends upon a wise selection and a skillful application of these methods, tools, and techniques, which, with the progress of the science, have become numerous and often intricate.

The present series is devoted to a comprehensive presentation of the techniques which are used in the organic laboratory and which are available for the investigation of organic compounds. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques. Reference is made to some investigations in the field of chemical engineering, so that the results may be of assistance in the laboratory and help the laboratory chemist to understand the problems which arise when his work is stepped up to a larger scale.

The field is broad and some of it is difficult to survey. Authors and editor hope that the volumes will be found useful and that many of the readers will let them have the benefit of their criticism and of suggestions for improvements.

A. W.

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TECHNIQUE OF ORGANIC CHEMISTRY

GENERAL PLAN

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TECHNIQUE OF ORGANIC CHEMISTRY

Volume V

ADSORPTION AND CHROMATOGRAPHY

PREFACE

It is the objective of this book to describe and explain, by discussion of principles, the various methods by which adsorption may be utilized in organic chemistry as a tool for the separation of mixtures. In the application of this tool the mixture is distributed between a bulk phase and the surface of a second phase, and the phases are chosen to yield, after separation, new systems enriched in one or more of the components of the original mixture.

To meet the purpose of this book it seemed necessary not only to describe the various ways in which adsorption may be used, but also to explain the nature of adsorption and of the phenomena associated with it (Chapters I and II). Other separation methods such as crystallization, distillation, extraction, and sublimation have been used more than adsorption chiefly because they are more thoroughly and widely understood and taught, and because the data necessary for their use—solubilities, melting points, boiling points, etc.—are more accessible or more easily estimated from chemical knowledge. There is, however, a great deal of information in the literature which can perform the same function with respect to adsorption and adsorbability. Some of it has been gathered, and limited generalizations have been drawn from it, in Chapters III, IV, and V, so that the chemist, operating from this material directly or by analogy, may be aided in solving problems of separation. Chapter VI, on the nature of separation processes, is significant in a slightly different sense: whereas Chapters III, IV, and V aid the experimenter in solving adsorption-separation problems by a consideration of the chemical and physical properties of phases, interfaces, and adsorptives, Chapter VI shows analogies with other separation processes.

The next four chapters describe and explain the various types of adsorption methods. The last chapter gives a few simple experiments by means of which the reader may familiarize himself with various techniques. There are also a few brief comments on the solution of problems. In this last group of chapters an effort has been made to deal with chromatography, ion exchange-adsorption, partition chromatography, etc. at the level of principle. The types of manipulations and the principles involved are explained as clearly as possible but, with the exception of the last chapter, no detailed procedures for specific separations are given. Obviously, the more detailed the direction the more restricted its use, and collections and excellent reviews of procedures and of specific applications of adsorption methods are available in the literature to which reference has been made. Ample space, however, has been given to the discussion of adsorbents and to compilations of their properties and sources.

Emphasis on the needs of the organic chemist has limited the discussion almost entirely to the properties and uses of liquid-vapor, liquid-liquid, and liquid-solid interfaces, but references to the literature on gas-solid or vapor-solid and other interfaces are given in Chapters I and II. Little discussion has been devoted to surface active agents, wetting and detergency, industrial applications of adsorption, or its historical aspects and biochemical implications, although references to the literature have been given where possible. The measurement of adsorption and of other properties at certain interfaces has been treated in Volume I of this series.

In his *Annotated Bibliography of Solid Adsorbents*, which covers the literature up to 1942, Deitz has listed some six thousand references. This represents only part of the literature in the much larger field of adsorption, and only someone who has attempted to read this literature can realize what an appalling task it would be to cover it completely. I have had to compromise and to look for what seemed to me to be important work and ideas. With the aims and limitations mentioned above I have, nevertheless, tried to cover a wide variety of phenomena and to show their connections with adsorption. If I have overlooked work which should have been included, I should appreciate hearing from readers of any such omissions, and I should likewise be most grateful for any other criticism and suggestions.

In certain of the chapters I have listed sources of materials and apparatus. The mention of special instruments or materials throughout this book does not imply that they are endorsed or recommended by me over others of a similar nature not mentioned. The listing is as complete as I could make it in this rapidly developing field.

I received my first introduction to adsorption and chromatography in the laboratories of Professor Harry N. Holmes, at Oberlin College, and I record here my debt to this inspiring teacher. Others have improved this book by criticism and suggestions. I express my thanks to Professor Henry C. Thacher, Jr., Dr. W. J. Knox, Jr., and the editor, Dr. Arnold Weissberger, who read the entire manuscript and made many valuable comments. Sections and chapters have gained in clarity and comprehensiveness thanks to Dr. E. M. Crane, Dr. P. H. Emmett, Dr. A. H. Frye, Mr. R. G. Haldeman, Mr. H. K. Inskip, Mrs. L. W. Inskip, Mr. G. N. Kowkabany, Dr. H. C. Thomas, Mr. V. Verplanck, and Mr. R. C. Zabor.

Chapter VI has been taken in large part from an article in the *Journal of Chemical Education,* May, 1950, with the kind permission of the editor, Dr. N. W. Rakestraw. Other parts of this book have been used in a graduate course in methods which I have taught since 1942. I have been materially aided by the facilities of the Yale University Libraries and of Berkeley College. I am indebted to Professor Samuel B. Hemingway for the latter. The library facilities of the Marine Biological Laboratory at Woods Hole were graciously placed at my disposal by Dr. Charles Packard. Finally, I acknowledge with pleasure the patient assistance rendered by the editor and publishers of this series. Other contributions, elsewhere acknowledged, have played important roles during the preparation of this book.

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December, 1950

TECHNIQUE OF ORGANIC CHEMISTRY

Volume V

ADSORPTION AND CHROMATOGRAPHY

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CHAPTER I

Definitions—Molecular Aspects of Adsorption

I. DEFINITIONS

A *system* is an assembly of phases. Each *phase* in any system is a distinct, homogeneous, macroscopic body which has a boundary and which can be separated by mechanical means from other parts of the system. The phase is macroscopically uniform in all internal directions: it is homogeneous bulk matter. The boundary between adjacent phases comprises an *interface,* in which the homogeneity of the phase has given way to a transitional inhomogeneity. Many properties which have fixed values in the bulk phase are found to change in value in the interface, and any of these properties may by virtue of this change in value be used to recognize and delineate the interface. When the interface is delineated through the measurement of *concentration,* then the phenomenon of adsorption may be recognized. Thus, a substance is said to be *adsorbed* if the concentration of the substance in a boundary region is higher than in the interior of the contiguous phases. (If the concentration of the substance is lower than in a contiguous bulk phase the substance is said to be *negatively* adsorbed.) *The definition of adsorption rests upon measurements of concentration, and carries no implication of mechanism.* A substance becomes adsorbed by a *process of adsorption,* or accumulation in a boundary region. The substance which is adsorbed is called the *adsorptive*; the *adsorbent* is the bulk phase (solid, or sometimes liquid) at the boundary of which the adsorption occurs. Sometimes the term *adsorbate* is applied to the substance which is adsorbed. However, this term is also used to mean the adsorbent *plus* the adsorbed substance, and it will be used only in the latter sense in this book, and sparingly.

Interface is in many ways a somewhat noncommittal term for the region in which two or more phases meet. In an actual system the properties of the interface may allow it to be characterized more specifically as an *interfacial film* or *interfacial phase* (for example, when it is fairly well marked off from the contiguous bulk phases). The more abstract term is useful in designating certain classes of boundaries, such as vapor–liquid interfaces, or gas–liquid–solid interfaces, etc. In any case, adsorption is a phenomenon of the interface, and is defined by measurements of concentration in the interface and the contiguous phases.

In the classical definition, adsorption (Γ) is defined (for the case of a boundary or surface between two phases) by:

$$\Gamma = \int_0^\infty [c(x) - c(\infty)]\, dx$$

in which c is a concentration, x is the distance from the "interfacial plane," and $c(\infty)$ is the concentration in the bulk phase outside of the interfacial region. The integration extends from the "interfacial plane" into the bulk phase. In this definition the "concentration" has the dimension moles per *square* centimeter. The "interfacial plane" is a geometrical surface (that is, with area but no volume), which separates the phases: The "interfacial plane" was defined by J. Willard Gibbs[1] *as an origin.* It may be placed somewhat arbitrarily within the physical interfacial region, which is then considered about this origin. This convention has received a very great deal of discussion.[2] A closer approach to the experimental picture would consider the interface as a region of uniform thickness separating the phases.[3] (See Chapter II.)

Interfaces may exist between two, three, or four phases. An interface between three phases is essentially linear; that between four phases is punctiform. These types will not be discussed to any great extent in this book. The interfaces formed by two phases are of several types which differ in properties among themselves: the liquid–gas, or liquid–vapor; the liquid–liquid; the solid–gas; the solid–liquid; and the solid–solid interfaces. The last of these is of no particular interest here. There are no gas–gas interfaces in the sense of the term used in this book, although a semipermeable membrane might deputize as an interface between two gases or other miscible phases.

An important feature of the interface between two phases is that its depth (or thickness) is ordinarily molecular in dimension (say 100 A., or less) while its extent (length and breadth) is macroscopic in dimension. The thickness of the interfacial region cannot be categorically stated. It was pointed out that many types of measurement may be made on a system which will give evidence of and delineate interfacial regions. More subtle measurements may show that the interfacial region extends farther into the contiguous phases than cruder measurements might reveal. Both the area and the thickness of the interfacial region are of importance in adsorption phenomena.

---

[1] J. W. Gibbs. *The Collected Works of J. Willard Gibbs,* Vol. I, Longmans, Green, New York, 1928, p. 219.

[2] E. K. Rideal, *An Introduction to Surface Chemistry,* 2nd ed., Cambridge Univ. Press, London, 1930; J. Rice, in *A Commentary on the Scientific Writings of J. Willard Gibbs,* Vol. I, F. G. Donnan and A. Haas, eds., Yale Univ. Press, New Haven, 1936, p. 542; Guggenheim and Adam, *Proc. Roy. Soc. London,* A139, 218 (1933); Guggenheim, *Trans. Faraday Soc.,* 36, 397 (1940) (this paper contains further references); N. K. Adam, *The Physics and Chemistry of Surfaces,* 3rd ed., Oxford Univ. Press, London, 1941; Defay, *Mém. acad. roy. Belg., Classe sci.,* 20, No. 6 (1946); Tolman, *J. Chem. Phys.,* 16, 758 (1948).

[3] For references, see Guggenheim, *Research,* Special Supplement, No. 2, 11 (1949).

Interfaces may be classified in two ways: as *mobile* and as *immobile*. Mobile interfaces include liquid–gas and liquid–liquid interfaces. These are characterized by an effective interfacial tension[4] under which the surface always tends to contract spontaneously. The molecules in mobile interfaces are continually being shuffled by the normal molecular motions of the fluid phases. The final state of the interface is thus a compromise: an equilibrium state in which the orienting forces of the interface are balanced by the shuffling effect of the molecular motions. This leads to the observable fact that mobile interfaces are usually homogeneous in directions parallel to their surfaces.

Immobile interfaces, on the other hand, are constrained by the rigidity of the solid phase, which forms at least one of the interface components. They include solid–gas, solid–liquid, and solid–solid interfaces. There are interfacial "tensions" here, but the interfaces may not contract because of their high viscosity. The opportunities for orientation in these interfaces are greater than those in mobile interfaces, for the solid phase contributes less fluidity, though even in solids there may be considerable molecular vibration and rotation. The immobile interface is further distinguished by the fact that it may be grossly inhomogeneous. It may differ in properties in different directions, as on the surface of anisotropic crystals; and it may be quite inhomogeneous in directions parrallel to the phase surfaces. These marked differences between mobile and immobile interfaces necessitate different treatments for them.

Adsorption takes place in the interface. The substance adsorbed may originate in one or more of the contiguous phases. The molecules of adsorptive pass from the phase into the interface, where they remain for a period of time. In a reversible process, the molecules can return to the phase from which they came, or can reversibly pass into another phase, their place in the interface being taken by other molecules. At equilibrium the number of molecules entering the interface in a given period of time is the same as the number of molecules leaving the interface. The requirement for adsorption is, according to the definition, *that the concentration of the substance in the interface be greater than that of the substance in the contiguous phases,* whether the concentration is calculated for unit area of interfacial plane and compared with unit area in the bulk phase, or is determined in some other way, as described in Chapter II.

[4] Bikerman, *J. Chem. Education,* 26, 228 (1949).

It is to be noticed that the operational definition of adsorption, based upon measurements of concentration, has certain important advantages. It makes no mention of the forces involved in adsorption. It will be pointed out that the accumulation of substances in interfaces may take place under driving forces that vary from the very weak to the very strong. The definition does not insist that the accumulation of excess substance in an interface be reversible. Reversibility is sometimes implied as one of the criteria of adsorption, but it is not a necessary requirement. The definition does not make any mention of the rates of adsorption. These may be quite different for different adsorptions. The speed of attaining equilibrium is not a characteristic of the phenomenon except in a general way, and is not a necessary part of a definition. The definition applies equally well for single- and multi-component systems. It permits a transition to other phenomena. For example, one of the phases involved may become subdivided more and more until its particles are of molecular dimensions, the phase character being lost in the process. The adsorbed substance under these circumstances, being also subdivided, also ends as molecules "associated" or otherwise combined with the quondam phase molecules. This may be visualized as a process of solution with adsorption at the solid surface.[5] On the other hand, the surface phase might increase in thickness until eventually it becomes macroscopic and homogeneous in all internal directions, thus becoming a true phase with its own boundaries. This situation may occur when gas liquefies on a solid or liquid surface, or when crystallization occurs from a solution onto a surface, the initial interfacial phase transforming into a bulk phase. Finally, as pointed out above, the definition makes no call upon mechanisms; it does not seek to define adsorption on the basis of a particular explanation. This leaves the subject open to various approaches and has the advantage of allowing a suitable but perhaps different approach to be taken to the several different aspects of adsorption phenomena again without undue emphasis upon the differences.

In any kind of adsorption study there are many concurrent and related measurable phenomena that may demand examination besides the actual adsorption itself. Thus questions may arise about the rate at which equilibrium is established, the average length of time during which a molecule remains adsorbed, the true reversibility of the process, the type of bond that exists between the adsorptive and the phase atoms, the change in energy that may occur in the process, the area occupied by the adsorbed molecule, the nature of the surface at the site of adsorption, the influence of neighboring adsorbed molecules on each other, the

[5] Calvet, *J. chim. phys.*, 35, 69 (1938); T. L. Hill, *J. Chem. Phys.*, 17, 507 (1949).

mobility along the surface shown by the adsorbed molecules, the extent of total surface covered by adsorbed molecules, the differences between covered and incompletely covered surfaces at equilibrium, the possible migration of adsorbed molecules into both phases, the possible formation of multimolecular films of adsorbed molecules, the effect of temperature, of concentration, and of other adsorbable atoms, on adsorption.

There are also subsidiary questions which may be raised; for example, must a substance remain chemically unchanged while accumulated in the interface for the phenomenon to be called adsorption? Again, it may be asked whether there is any scope in the adsorption phenomenon for the operation of stoichiometric laws; of some simple numerical relation between the number of molecules adsorbed and the number in the adsorbing surface. A question may be raised about what effect the roughness of a surface has on adsorption, and in general what the topological factors are that influence adsorption, and how they operate.[6]

It may be emphasized, further, that adsorption is not the only property shown by an interface. That is to say, there are many kinds of differences between an interface and a phase other than a concentration difference. For example, there is a difference in arrangment of molecules; in density; in free energy; and in other properties. Some of these differences can be more readily measured than differences in concentration, and it is therefore important to correlate them with adsorption (Chapter II). Again, the various properties of the interfacial region, while different from those of the bulk phases, are nevertheless dependent upon them. Thus temperature and pressure or concentration of the bulk phases influence the interface and its properties, including adsorption. The properties of the components of the phases—the chemical natures of the molecules present; their interactions that affect solubility, vapor pressure, heat of solution, evaporation, and crystallization; etc.—represent another class of properties that affect the interface. Those properties are exceedingly important because any correlations between them and adsorption permit predictions and estimates of probable adsorption behavior. The examination of the effect of chemical structure upon adsorbability is therefore of great practical and theoretical importance. In general, then, there are three classes of properties of a system which may to different degrees be correlated with adsorption: the other properties of the interface (Chapters I and II); the properties of the bulk phases (Chapter III); and the properties of the adsorptive molecules (Chapter IV). These classes are not mutually exclusive.

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[6] J. J. Bikerman, *Surface Chemistry for Industrial Research.* Academic Press, New York, 1947.

II. ENERGY OF ADSORPTION

The definition given for interface does not imply adsorption but only discontinuity at the mutual boundary of two phases. However, because of the forces operating between the phases, virtually all interfaces, with the common exception of the surfaces of pure liquids, must in actual experience show adsorption phenomena. These forces, or interactions, are a function of the matter which constitutes the phases. The interactions involved in adsorption run the gamut from the most tenuous physical interactions and van der Waals forces to those strong bonds which it is convenient to designate as chemical. There is no special type of force, or strength of interaction, that may be designated exclusively as an adsorption force. For this reason, adsorption has purposely been defined without reference to the forces that may bring it about.

All adsorption processes involve a decrease in the free energy of the system. All adsorption processes are exothermic. The decrease in the heat content of the system is called the *heat of adsorption.*

In dealing with adsorption at solid surfaces, the magnitude of the energy of adsorption has frequently been used as a basis for classification of the adsorption processes. Thus processes in which the energy changes are small have been classified as *van der Waals,* or *physical, adsorptions,* and those in which the energy changes are much greater are frequently designated as chemical adsorptions, or *chemisorptions.*[7] The difference between these two types of adsorption is, according to this method of classification, that the former involves heats of the order of those found in the liquefaction of gases; the latter involves heats of the order of those found in chemical reactions. This classification would not break down if the heat of adsorption were found to have some intermediate value: if it could be shown that in these cases the two clearly different types of adsorption were occurring simultaneously. The terms van der Waals adsorption and chemisorption have great utility, but cannot reasonably be too rigidly defined. Van der Waals adsorption involves relatively small energy changes; chemisorption relatively large ones. But adsorptions could be found with energy changes between these limits, indeed running the whole gamut, and it would be difficult in many cases to say with conviction that chemisorption begins at any particular portion of the scale.

Activated adsorption is the name commonly used for adsorptions (chiefly on solid adsorbents) which take place slowly, and at a temperature not too far above room temperature.[8] Here it is conceived that for the adsorption to occur some sort of potential barrier must be surmounted by the molecules, so that only those with sufficient energy can become adsorbed. The energy distribution of the molecules in a phase at room temperature may be such that only relatively few molecules at a given time contain the energy requisite to surmount this barrier, hence the slowness of the reaction. The rate of the reaction here would increase with rise in temperature.[9]

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[7] For a review, see S. Brunauer, *The Adsorption of Gases and Vapors,* Vol. I, *Physical Adsorption,* Princeton Univ. Press, Princeton, 1943.

It is seen, therefore, that like so many descriptive terms in chemistry, van der Waals adsorption, activated adsorption, and chemisorption cannot readily be given any sharp quantitative significance. There will be borderline cases of adsorption any classification of which will be open to question. Such cases can best be left unclassified since their distinctions have ceased to be useful. One can agree with Hartley, however, that it is profitable to examine the reasons for the failures of the distinctions.[10] In this case the reason is clear: one distinguishes between high and low values of a function (energy of adsorption) for which a range of values, including intermediate ones, can be found.

III. MOLECULAR ASPECTS OF ADSORPTION

When adsorption occurs from a mixture of substances (a situation that is of great importance as far as this book is concerned), there is a competition between the various adsorptives for the interface. Under these conditions the geometry of the interface, and of the molecules of adsorptive, as well as the chemical and physical properties of the molecules of adsorptive and adsorbent, play important roles in the process. Indeed, some prediction of relative extent of adsorption can often be made from a knowledge of these properties. The relations of these properties of molecules to relative extent of adsorption are considered in later chapters. Here a more general picture is drawn of the molecular aspects of adsorption.

1. Solid–Gas or Solid–Vapor Interface

As explained in the preface, adsorption to the surface of a solid from a gas phase, though of considerable theoretical and practical importance, is not treated in this book except briefly in connection with other interfaces. A knowledge of the behavior of the gas–solid interface is helpful in understanding phenomena in others, since *relatively* simple systems can be dealt with. Some aspects of the measurement of adsorption at this interface are discussed in the following chapter. Many monographs are available on this subject.[11] Practical aspects are mentioned in Chapter VII, but only in passing.[12]

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[8] Taylor, *Chem. Revs.*, 9, 1 (1931); N. K. Adam, *The Physics and Chemistry of Surfaces*, 3rd ed., Oxford Univ. Press, London, 1941, p. 252.

[9] For a discussion of activation energy of adsorption at mobile interfaces, see Ward and Tordai, *Nature*, 154, 146 (1944); Ward, *Research*, Special Supplement, No. 2, 55 (1949).

[10] Hartley, *Aqueous Solutions of Paraffin Chain Salts. A Study of Micelle Formation*. Hermann, Paris, 1936, p. 14.

2. Vapor–Liquid Interface

A. PURE LIQUID

The interfacial region between a liquid and its vapor, or at the air–liquid interface, must be a region of rather abrupt transition. In the case of a pure liquid in equilibrium with its vapor the surface phase can differ from the contiguous phase only in structural arrangement of the molecules[13] and in density. If, however, the pure liquid contains more than one kind of molecule[14] (as in the case of associated liquids) or of particle (as in the case of dissociated liquids) the surface phase could differ also in concentration, as well as in other ways.[15]

The surface of even a pure liquid is conceived to show a certain structure. Thus Langmuir,[16] on observing that the total surface energy of a number of normal saturated aliphatic alcohols is about the same as that of hexane (about 50 ergs/cm.^{2}), concluded that the surfaces of these liquids must be largely hydrocarbon in nature. This suggested a certain orienting effect which constrains the molecules in the surface, so that although they are in thermal motion the polar groups do not, for any appreciable fraction of the time, form part of the free surface of the liquid. Further evidence for the orientation of molecules in the surfaces of pure liquids has been advanced by Harkins.[17] He has pointed out that saturated aliphatic acids and alcohols show about the same energies of cohesion as hydrocarbons. The increase in internal energy which occurs when a "cylinder of pure liquid"[17] is "pulled apart" to give two new surfaces each one square centimeter in area (this is not an actual experimental procedure) is, in ergs per square centimeter, given in Table I-1. Since the energy of cohesion of water is 233 ergs/cm.^{2} then evidently in the case of the acids and alcohols the polar end groups must not contribute very much to the new surfaces. The new surfaces can be expected to be formed with the least possible free energy content. Thus orientation must occur in their formation and they must be largely hydrocarbon in nature. The orientation is thought to be brought about through interactions of the polar functional groups. This subject was discussed in the pioneering papers of Langmuir[18] and Harkins,[19] and has been treated to some extent in Volume I of this Series.[20]

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[11] S. Brunauer, *The Adsorption of Gases and Vapors*, Vol. I, *Physical Adsorption*, Princeton Univ. Press, Princeton, 1943; J. K. Roberts, *Some Problems in Adsorption*, Cambridge Univ. Press, 1939; A. R. Miller, *The Adsorption of Gases on Solids*, Cambridge Univ. Press, New York, 1949.

[12] C. L. Mantell, *Adsorption*, McGraw-Hill, New York, 1945; E. Ledoux, *Vapor Adsorption*, Chemical Pub. Co., Brooklyn, 1945.

[13] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*. Macmillan, New York, 1939, p. 421.

[14] Cassidy, *J. Chem. Education*, 26, 335 (1949).

[15] McBain and Mills, *Repts. Progress Phys.*, 5, 30 (1939).

[16] Langmuir, *Colloid Symposium Monograph*, 3, 48 (1925).

[17] Harkins, in *Surface Chemistry*, Publication 21, Am. Assoc. Adv. Sci., Washington, 1943, p. 46; Harkins, Clark, and Roberts, *J. Am. Chem. Soc.*, 42, 700 (1920).

TABLE I–1

Energy of Cohesion for Different Types of Substances in Ergs per Square Centimeter[17]

Acids	Alcohols	Paraffins
	n-Octyl........101	*n*-Octane........100
Heptanoic......105		*n*-Heptane......100
	Butanol........97	*n*-Butane........92
	Propanol........96	Propane.........68
	Ethanol........97	
	Methanol.......98	

It must not be thought that the orientation which would seem to exist, in some cases at least, at the surface of a pure liquid can be such that the molecules are packed closer together. The molecules in the bulk liquid are closer together than they are in the vapor above the liquid, and the transition between the two phases is found to be quite a sharp one. The evidence seems to indicate that within the transitional, interfacial region of the pure liquid there is a sharp change of density: a diminution toward the gas phase.

B. VAPOR—SOLUTION INTERFACE

Soluble, Surface-Active Solute. With solutions, the molecular aspects of adsorption are in some ways easier to picture. It is clear that if two molecular species are present the concentration of one in the interface might be greater or less than its concentration in the bulk solution. This is because the ratio of the numbers of the two kinds of molecules per unit area or volume is the important consideration in this case. With a pure liquid the only way concentration could increase at the interface would be by a compression of the molecules: an increase in the number of molecules per unit volume of the liquid, and this does not seem to occur. With a solution, adsorbed solute could replace solvent molecules without necessitating a change in the number of molecules per unit volume of interface. Indeed, if the adsorbed solute molecule were large it might displace many solvent molecules, so that with increase in solute concentration at the interface there might be an actual decrease in the total number of molecules per unit volume of interface. The converse of this is also possible.

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[18] Langmuir, *Chem. Met. Eng.*, 15, 469 (1916); *J. Am. Chem. Soc.*, 38, 2221 (1916); 39, 1848 (1917).

[19] Harkins, Brown, and Davies, *J. Am. Chem. Soc.*, 39, 354 (1917); Harkins, Davies, and Clark, *ibid.*, 39, 541 (1917).

[20] Physical Methods of Organic Chemistry, 2nd ed. A. Weissberger, Ed., Interscience, New York, 1949, Part I, pp. 360–361.

When a small amount of fatty acid (or for that matter any monofunctional aliphatic substance) is dissolved in water it is found that the acid is adsorbed at the surface of the solution with a lowering of surface tension. Many attempts have been made to relate this surface tension lowering, or *capillary activity,* to the concentration of the solute in the bulk solution, and to relate the capillary activity to the molecular structure of the substance. The result of some of this early work was to show that the capillary activities of members of certain homologous series increased regularly (in a geometrical progression) with each added CH_2 group in the chain,[21] the capillary activity being measured as the slope of the initial, nearly straight part of the surface tension–concentration curve. The statement of this regular increase in capillary activity is known as *Traube's rule.*

Langmuir[22] interpreted these and other data to mean that as longer chains were taken each additional CH_2 group occupied in the surface a position similar to that of the other CH_2 groups; in other words, that the hydrocarbon parts of the adsorbed molecules were spread out in the surface of the dilute solutions. Data bearing on this conclusion have been collected by Adam.[23]

Ward[24] reexamined these data and arguments in the light of more recent information and came to the conclusion that as far as the lower, soluble fatty acids are concerned the concept that the chain was spread out flat in the surface of dilute solutions could not be supported. Ward pointed out that when a molecule of a soluble fatty acid moves from the bulk solution into the surface the essential change is that the hydrocarbon part passes from an entirely aqueous environment to a state where it is in contact with both water and air. The carboxylic acid group always remains in the water phase and thus undergoes no change on adsorption. Virtually only undissociated molecules are adsorbed at the surface[25] and this makes the concentration of adsorbable molecules lower than the stoichiometric concentration by a factor which can be calculated from the dissociation constant of the acid. (This restriction may not be universally valid. Rehbinder[26] found tetraalkyl ammonium salts to be adsorbed at the surface of aqueous solutions in which they are presumably completely ionized; also many highly ionized surface-active substances are known.[27])

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[21] Traube, *Ann.,* 265, 27 (1891); von Szyszkowski, *Z. physik. Chem.,* 64, 385 (1908).

[22] Langmuir, *J. Am. Chem. Soc.,* 39, 1848 (1917).

[23] N. K. Adam, *The Physics and Chemistry of Surfaces.* 2nd ed., Oxford Univ. Press, London, 1938, pp. 57–58.

[24] Ward, *Trans. Faraday Soc.,* 42, 399 (1946).

The molecule of fatty acid in solution is probably curled up most of the time, so that the minimum surface area is presented to the water, and the minimum surface energy is thus achieved.[28] This would involve the assumption of a spheroidal form.[29] It is unlikely, then, that the fatty acid on moving into the surface would stretch out. It would rather be expected to retain the curled-up shape—a restriction being present, however, that whereas in the bulk phase the molecule with its projecting carboxylic group can rotate rather freely, in the surface the carboxylic group remains always in the water phase. This is the restriction postulated by Langmuir.

Ward showed how the fall in the potential energy of the molecule in passing into the surface varies with the number of carbon atoms in the hydrocarbon part of the chain. If the molecules were to lie half-immersed in the surface, then the energy would equal

$$^1/_2 \text{ surface area of molecule} \times 51 + {}^1/_2 \text{ surface area of molecule} \times 31 \\ - \text{cross-sectional area} \times 72.8$$

in which 51 is the interfacial tension (in dynes per centimeter at 20°) between paraffin hydrocarbons and water, and 31 is the limiting value of the surface tension (dynes per centimeter at 20°) of paraffin hydrocarbons (and of liquid fatty acids) reached with long chains. This limiting value is used because thermal agitation of a long hydrocarbon chain in the surface will mainly cause the breaking of contacts between different parts of the same molecule, and in considering the exposed hydrocarbon part of the single molecule the contacts between different groups along the surface of the molecule are intramolecular. The last term in the statement is due to the water surface which is destroyed when the fatty acid moves into the interface, the surface tension of water being 72.8. The energy of the molecule in the surface at the position of lowest potential energy must actually be some 6.1% lower than that calculated for half-immersion, because the molecule will tend to rise higher into the air since the hydrocarbon–air surface energy is lower than the hydrocarbon–water surface energy. The equilibrium position, however, is not much above the line of half-immersion, since at the same time that the molecule rises the water surface destroyed becomes less.

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[25] Lottermoser and Winter, *Kolloid-Z.*, 66, 276 (1934).

[26] Rehbinder, *Z. physik. Chem.*, 111, 447 (1924).

[27] A. M. Schwartz and J. W. Perry, *Surface Active Agents*. Interscience, New York, 1949.

[28] Langmuir, in J. Alexander, *Colloid Chemistry*. Vol. I, Reinhold, New York, 1926, p. 525.

[29] Treloar, *Proc. Phys. Soc. London*, 55, 345 (1943).

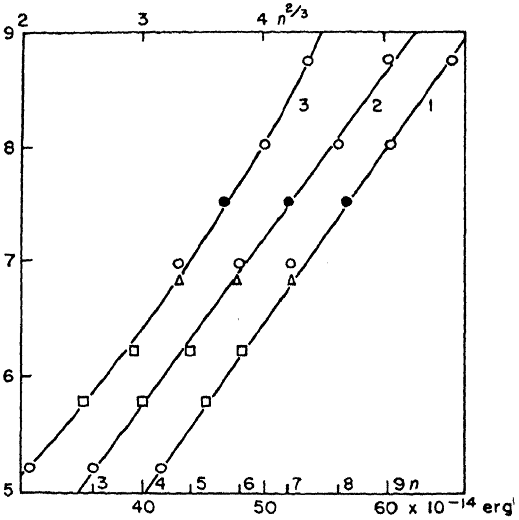

Fig. I-1. Log a, which is directly related to the fall in potential energy of the molecule in passing from the solution into the interface, is plotted on the ordinate.[24] The abscissa for curve *1* is the free energy change, in ergs; for curve *2* it is n, the number of carbon atoms in the hydrocarbon chain of the molecule; and for curve *3* it is $n^{2/3}$. The data are from King, *Kansas Agr. Expt. Sta. Tech. Bull.*, No. 9 (1922) (○); v. Szyszkowski, *Z. physik. Chem.*, **64**, 385 (1908) (□); Weber and Sternglanz, *ibid.*, **A169**, 241 (1934) (△); and Frumkin, *ibid.*, **116**, 498 (1925) (●).

The fall in potential energy of the molecule as it becomes adsorbed thus depends on its surface area. If the molecule were in the stretched-out, cylindrical form, the cross-sectional area of the hydrocarbon part being independent of the chain length, then the surface area would increase linearly with the number (n) of carbon atoms. If the molecule were in the form of a sphere its area would be proportional to $n^{2/3}$. A plot of the fall in potential energy on adsorption against n should give a straight line for stretched-out molecules and a straight line against $n^{2/3}$ for spherical molecules. For fatty acids the plot is a straight line for n, and a curve with $n^{2/3}$ (Fig. I-1). This was the observation which led Langmuir to conclude that the molecules in these dilute solutions must be spread out flat in the surface.

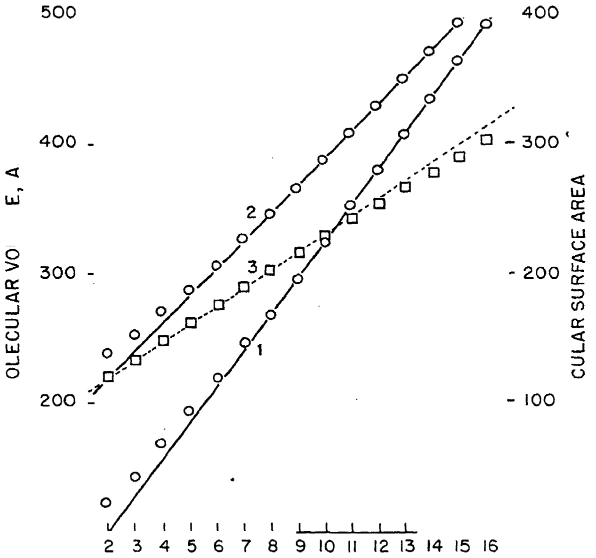

Fig. I-2. The number of carbon atoms in the chain of the paraffin hydrocarbon is plotted on the abscissa.[24] The ordinate for curve *1* is molecular volume; for curve *2* it is area of the molecule as a cylinder; for curve *3* it is area of the molecule as a sphere.

Ward showed, however, that by a coincidence the observed molecular volumes of the hydrocarbons up to about $n = 8$ or 9 have such values as to make the areas of the molecules taken in the form of spheres vary almost linearly with n, and not with $n^{2/3}$ (Fig. I-2). He used the hydrocarbon for reference because this is the part of the fatty acid molecule $H(CH_2)_nCOOH$ that is in the surface. "It therefore happens," he says, "that by making the reasonable assumption that the hydrocarbon groups are in the form of spheres both in the bulk and on the surface we obtain equal increments in area (and therefore in energy) in passing along the homologous series up to about C_8H_{18}. The truth of Traube's rule is thus dependent upon this accidental circumstance." Since hydrocarbons above C_8H_{18} behave regularly as regards molecular volume, their surface areas would be proportional to $n^{2/3}$, not n, and acids corresponding to these should, were they soluble in water, not obey Traube's rule. A test of this is not at present possible, but Ward adduced in support of his hypothesis the values found by Huggins[30] for the latent heats of evaporation of hydrocarbons. Huggins found that the latent heat of evaporation of hydrocarbons varies linearly with $n^{2/3}$ for hydrocarbons above C_8H_{18} but not for the lower hydrocarbons. This agrees with the concept that the cohesional energy of the molecules in the liquid is proportional to the area of the molecules, and that in passing into the gas the molecule breaks contacts with its neighbors in the liquid over this whole area. (In the gas phase the surface energy of the molecule is also proportional to its surface area.) The surface area, then, would be expected to vary linearly with $n^{2/3}$ for these hydrocarbon molecules above C_8H_{18}, and Traube's rule would not be followed for acids (and other polar substances) with side chains of C_8 or above.

Neglecting the polar end groups, the chains in the surface, being hydrocarbon in nature and short in length, may as a first approximation be considered to be unaffected by the solvent, and at this dilution by each other. That they are relatively unaffected by each other is suggested by the observation that at high surface dilutions (a large area of the surface being available for each molecule) these molecules obey a "two-dimensional gas law" for a perfect gas, *i.e.*, $\pi\sigma = kT$. Here π is the surface pressure, the difference between the surface tension of the pure solvent and that of the solution, and is analogous in two dimensions to ordinary pressure in three. The area per molecule, σ, takes the place of volume.[31] If the concentration of the solute is increased without increasing the interfacial area, then as more molecules become available their concentration in the interface will increase with concomitant displacement of water molecules and lowering of surface tension. As long as the interfacial area is very large compared with the number of acid molecules in it this increase is almost directly proportional to the concentration of molecules in the bulk phase, which is why the initial part of the surface tension–concentration curve is almost a straight line (Fig. II-5). At high dilution the analogy of the film behavior to that of a gas in two dimensions is much better than one might at first expect. This may be because of the great mobility of the water molecules.[32]

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[30] Huggins, *J. Phys. Chem.*, 43, 1083 (1939).

[31] N. K. Adam, *The Physics and Chemistry of Surfaces*, 2nd ed., Oxford Univ. Press, London, 1938, p. 40 *et seq.*; Langmuir, *J. Am. Chem. Soc.*, 39, 1848, 1888 (1917); Adam and Jessop, *Proc. Roy Soc. London,* **A110,** 423, 424 (1926).

If the concentration of the solute is further increased, the number of molecules in the interface also increases. The relative area of interface taken over by these molecules also increases, but the total area of the interface is constant and hence the number of water molecules in the interface decreases. Now, as the acid molecules occupy larger proportions of the interfacial region so that on the average they come closer to each other, they behave less like a perfect gas. As the "available space" in the interface decreases, the concentration of acid molecules in the interfacial region increases continually less rapidly than in the bulk water phase, and there is no longer the original, nearly linear relation between increase in concentration of the solution and increase in adsorption. Instead the relation becomes an exponential one; the exponent which was 1 in the linear relation changes to values less than 1. At the limit the entire interfacial area, or substantially the entire area, consists of a layer of molecules of the acid: the surface is saturated.

Before the point of complete saturation is reached the tendency of the crowded molecules to adhere to each other becomes evident: as the surface "two-dimensional pressure" increases, a partial "two-dimensional condensation" occurs.[33] Langmuir[34] has concluded on theoretical grounds that the molecules in such films are in contact, but not wholly oriented, and that the carboxyl, or other polar, groups of the film molecules are directed toward the water phase, the hydrocarbon portions lying on the water toward the air phase. The phenomenon was investigated by Langmuir[35] using the data of Traube[36] and Szyszkowski[37] for surface tensions of aqueous solutions of fatty acids and other aliphatic substances. The adhesion between the hydrocarbon chains reaches its greatest effectiveness when they are relatively long, but it still must exist in diminished degree in the lower members of the aliphatic series under these conditions of crowding.

In the concentrated solutions, where the surface is saturated, or nearly so, the amount of fatty acid adsorbed becomes virtually independent of the concentration in the bulk phase. Not only that, but the number of molecules in a given unit of area at the point of saturation of the surface is the same for the four acids propionic, butyric, valeric, and caproic. Thus the areas occupied by all these molecules are the same; the length of the chain does not influence the extent of adsorption under these conditions. Langmuir concluded that the only reasonable arrangement that would account for these findings is one in which the molecules are vertically placed or inclined in the film, the carboxyl groups are in contact with the water and the hydrocarbon chains are extended. Under this arrangement increased length of the chain would not change the area occupied in the film by the molecule but would only increase the thickness of the film. Such increase in thickness has been shown to occur. It should be mentioned that the cross-sectional area of the molecule as judged by the area it occupies in these fully saturated films varies depending upon the nature of the molecule, its shape, and the size and number of polar groups.

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[32] Adam, *Proc. Roy. Soc. London,* **A101**, 516 (1922).

[33] N. K. Adam, *The Physics and Chemistry of Surfaces,* 2nd ed., Oxford Univ. Press, London, 1938, p. 39.

[34] Langmuir, *Colloid Symposium Monograph,* **3**, 48, 74 (1925); *J. Chem. Phys.,* **1**, 756 (1933).

[35] Langmuir, *J. Am. Chem. Soc.,* **39**, 1848, 1890 (1917).

[36] Traube, *Ann.,* **265**, 27 (1891).

[37] von Szyszkowski, *Z. physik. Chem.,* **64**, 385 (1908).

Calculations by Harkins and Wampler[38] are of interest in completing this description. Adsorption of butyl alcohol at the surface of aqueous solutions was calculated from the surface tension of the solution by means of the Gibbs equation (Chapter II). Their data and calculated results are given in Table I-2. It must be evident from these data that with increased concentration of the solution the packing of solute in the interfacial region increased, with continually decreasing surface area available per molecule of solute. The area per molecule of alcohol in the film at the highest concentration measured was 23.7 A.^{2} In films of insoluble long-chain alcohols, where the packing can be tighter since the molecules cannot escape into solution, the cross-sectional area found

TABLE I-2
Adsorption of Butyl Alcohol at Solution–Gas Interface

Molality	Surface tension	Moles per cm.^{2} $\times 10^{10}$	Area per molecule adsorbed, A.^{2} (25°).
0.00329	72.80		
0.00658	72.26		
0.01320	70.82	1.26	132
0.0264	68.00	2.15	76
0.0536	63.14	3.54	47
0.1050	56.31	4.72	35
0.2110	48.08	5.26	31.4
0.4330	38.87	5.69	29.0
0.8540	29.87	6.03	27.4

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[38] Harkins and Wampler, *J. Am. Chem. Soc.*, 53, 850 (1931).

per molecule is 21.6 A.[2] Frumkin, Gorodetzkaja, and Tschugunoff[39] found that saturation occurred at the caproic acid solution—air interface at about 6×10^{-10} mole/cm.[2] This is in good agreement with the value at the highest concentration measured by Harkins and Wampler.

After the surface has been virtually saturated with acid molecules the concentration in the water layer may increase without any substantial increase in adsorption until the water phase becomes saturated. At this point the acid molecules begin to "pile up" at the interface, and as more acid is added to the system the insoluble excess accumulates at the interface and finally becomes a separate phase with its own boundaries. But at the interface between the acid phase (containing dissolved water) and the water phase (containing dissolved acid) adsorption may be expected to occur. This extreme case has been described by Hildebrand[40] in another connection: "When positive deviations from Raoult's law become very large they lead to the formation of two liquid phases. The formation of a second liquid phase upon the surface of a first may also be regarded as a case of very extreme adsorption." This general idea was also used by Langmuir.[41] He treated the adsorbed layer of aliphatic (acid) molecules on the surface as if it were composed of a hydrocarbon phase lying on a water phase, with the polar groups, equal in number to the adsorbed molecules, interposed at the hydrocarbon—water interface. At this stage, where the solution becomes saturated with solute so that further added solute separates as a bulk phase, we have the transition to the case of adsorption at the interface between two liquid phases. It must be restated that, though the above picture has been drawn taking fatty acids as the adsorptives, essentially the same picture (except for possible effects of dissociation) would have had to be drawn had any other normal monofunctional aliphatic substances, such as alcohols, methyl esters, aldehydes, methyl ketones, amines, nitriles, etc., been taken as the adsorptives.

A number of other phenomena are observed at the surface with soluble capillary-active adsorptives. When a new surface is formed it requires a finite period for the surface tension to reach a constant value. The period required may be very short, of less than 0.005 sec. duration with pure liquids,[42] or it may be quite long. A. E. Alexander has reviewed the data and the theories which have been advanced to explain the slow aging of some surfaces.[43] He has concluded that the rate-determining step in the process is the penetration of the hydrophobic portion of the surface-active molecule into the surface and its reorientation there. The slow aging is often, but not always,[44] eliminated at an oil–water interface.

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[39] Frumkin, Gorodetzkaja, and Tschugunoff, *Acta Physicochem. U. R. S. S.*, 1, 12 (1934).

[40] J. H. Hildebrand, *Solubility of Non-Electrolytes*. Reinhold, New York, 1936, p. 191.

[41] Langmuir, *J. Chem. Phys.*, 1, 756 (1933).

[42] Bond and Puls, *Phil. Mag.*, 24, 864 (1937).

The electrical and other properties of surface films have been treated by Harkins in Volume I of this series, and by others.[45,46]

Soluble, Nonsurface-Active Solute. Some very soluble substances are known, the solutions of which show surface tensions slightly higher than those of the pure solvents. These substances are negatively adsorbed at the surface. A molecular picture of this behavior is difficult to give, but one may suppose that these substances, which are very soluble and in some cases highly ionized in water are able, by their strong interaction with the solvent, to bind the solvent molecules so as to decrease the diffuseness of the interfacial transition zone and thus sharpen the discontinuity at the boundary of the solution. The types of data obtained with these substances are described in Chapter II.[45]

Insoluble Adsorptive. With slightly soluble solutes the solution can become saturated *before* the interface is filled with molecules of adsorptive. The phenomena which can manifest themselves under these conditions have furnished the subject matter of a rather extensive literature.[46]

When the substance adsorbed at a vapor–liquid interface is not appreciably soluble in the liquid phase and is practically nonvolatile, a special situation arises: the surface film which may be formed becomes more tangible, so to speak, than that of a soluble adsorptive. Solution molecules adsorbed at a vapor–liquid interface are able to diffuse back into the bulk liquid phase and, if volatile, to escape into the vapor phase. The same molecules are undoubtedly not present in the interface all of the time. On the other hand the molecules of a nonvolatile substance in a surface film cannot escape into the vapor phase, and if at the same time they are not very soluble, then they are largely confined to the surface. They exhibit their own thermal motion and are subject to that of the superficial molecules of the underlying liquid. They can diffuse laterally, perhaps, and they can condense into droplets and crystals depending on whether they will form liquid or solid when in bulk, but they cannot escape freely.

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[43] A. E. Alexander, *Trans. Faraday Soc.*, 37, 15 (1941).

[44] Ward, *Research*, Special Supplement, No. 2, 55 (1949).

[45] N. K. Adam, *The Physics and Chemistry of Surfaces*, 3rd ed., Oxford Univ. Press, London, 1941; A. E. Alexander and P. Johnson, *Colloid Science*, Oxford Univ. Press, London, 1949; A. M. Schwartz and J. W. Perry, *Surface Active Agents*, Interscience, New York, 1949.

[46] E. K. Rideal, *An Introduction to Surface Chemistry*, 2nd ed., Cambridge Univ. Press, London, 1930; Langmuir, Pilgrim Trust Lecture, *Proc. Roy Soc. London*, A170, 1 (1939); Dervichian, *J. Chem. Phys.*, 7, 931 (1939); N. K. Adam, *The Physics and Chemistry of Surfaces*, 3rd ed., Oxford Univ. Press, London, 1941, Chap. II; Harkins, in Weissberger, *Physical Methods of Organic Chemistry*, 2nd ed., Interscience, New York, 1949, Part I, pp. 427–485.

In work with these interfaces it is convenient to measure film pressure (π) rather than surface tension, and to replace the concentration, useful for a soluble adsorptive, with the area (σ) available per molecule placed on the surface. In dilute films the area available per molecule will, of course, be large. The film pressure is the difference between the free surface energy of the clean surface and of the film-containing surface. The methods of measurement and some interpretation of results are given by Harkins in Volume I of this series.[47] The books by Adam,[48] Bikerman,[49] and Alexander and Johnson[50] survey the subject. In essence, the surface film is manipulated by means of barriers which may be adjusted in the surface, and the pressure exerted by the film is measured with a torsion or other balance.

It was pointed out by Langmuir[51] that with a small amount of soluble, capillary-active substance in a given area of the water interface the decrease in surface tension from that of the pure solvent might be quite large, say 17.5 dynes/cm., whereas with the same number of molecules of a substance such as palmitic acid on the surface the change in surface tension would be rather small, less than 0.2 dyne/cm. This difference is laid to the strong lateral forces between the palmitic acid molecules and to their insolubility in the water. This phenomenon, together with the influence of the solvent on adsorption at the air–solution interface, has been studied by many investigators, among whom may be mentioned Frumkin[52] and Taubman.[53–55] From studies of the relative abilities of a variety of polar and nonpolar molecules to lower the surface tensions of water, nitrobenzene, and other solvents it was concluded that the solvent certainly played an important role in the extent of the adsorption; however, it alone was not necessarily dominant.

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[47] *Physical Methods of Organic Chemistry,* 2nd ed., Part I, pp. 355–413.

[48] N. K. Adam, *The Physics and Chemistry of Surfaces,* 3rd ed., Oxford Univ. Press, London, 1941, Chap. II.

[49] J. J. Bikerman, *Surface Chemistry for Industrial Research.* Academic Press, New York, 1947.

[50] A. E. Alexander and P. Johnson, *Colloid Science,* Vols. I and II, Oxford Univ. Press, New York, 1949.

[51] Langmuir, *J. Am. Chem. Soc.,* **39,** 1848, 1888 (1917).

[52] Frumkin, *Z. physik. Chem.,* **116,** 466 (1925).

[53] Rehbinder and Taubman, *Z. physik. Chem.,* **147,** 188 (1930).

[54] Taubman, *Z. physik. Chem.,* **161,** 129 (1932).

[55] Taubman, *Compt. rend. acad. sci. U. R. S. S.,* **29,** 22, 103, 210, 213 (1940).

When small polar molecules (acetic acid, 1-propanol, etc.) are dissolved in water they lower the surface tension to an extent which increases regularly with the concentration. However with substances of higher molecular weight, beginning at about C_8, or perhaps even C_6 in the fatty acid series, the curve of surface tension lowering versus concentration begins to show an inflection which becomes more marked with increase in chain length of the molecule until at C_{12} the change in surface tension with concentration is nearly zero for the initial portion of the concentration curve (Fig. I-3). This was interpreted by Frumkin[52] as indicating that the *nonpolar* parts of the molecules (the hydrocarbon chains) show an attraction for each other which is greater than their attraction for water. This mutual attraction manifests itself when the chains are sufficiently long: the molecules cohere in such numbers that the net effect in lowering surface tension is decreased.

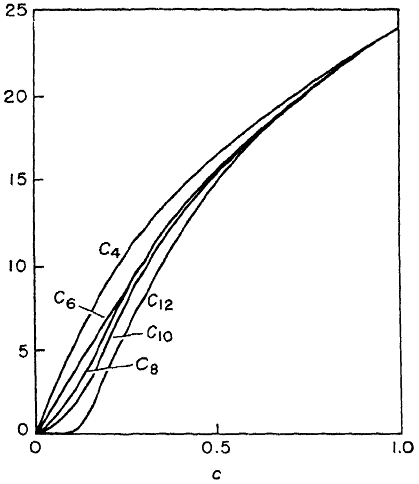

Fig. I-3. Schematic representation of the surface tension lowering (Δ) with concentration (c) for aqueous solutions of aliphatic substances (acids, alcohols, etc.) with polar end groups.[52] The inflection appearing with the longer chain compounds (from about C_8 on) is shown.

The idea was applied by Taubman[55] to the interpretation of the curves for change of surface tension with concentration of substances dissolved in nitrobenzene. The isotherms found for a number of hydrocarbons (benzene, naphthalene, cetylbenzene, hexane, decane, cetene, cyclohexane) and diethyl sebacate, showed no inflection even with the long-chain compounds. On the other hand, *n*-butyl and *n*-octyl alcohol, *n*-butyric acid, and ethyl caprinate did show the S-shaped inflection. The interpretation was that the interaction of the nitrobenzene with the hydrocarbon chains (solvation) was sufficient to counter the attraction between chains, and that with diethyl sebacate the additional anchoring effect of the symmetrically placed polar groups contributed to this horizontal orientation. The interpretation was supported by calculations of the minimum area available per molecule at saturation and the thickness of the surface layer (obtained from the Gibbs equation). The activities of the substances were determined by cryoscopic measurements of the lowering of the melting point at the different concentrations. From these calculations it appeared that the substances which showed no inflection in the low-concentration part of the curve were those which lay flat on the surface. These formed films which even at saturation of the surface were of the same order of thickness as would be expected of a molecule lying with its long axis in the surface. The substances which showed inflections also gave thicker films, consistent with the interpretation that they were to a considerable extent up-ended in the film. Measurements were extended[55] to aqueous solutions, using molecules with two functional groups (dibasic acids and esters, and glycols). The lower members of the series gave uninflected isotherms, but pimelic, azelaic and sebacic acids, and decamethylene glycol showed evidence of inflection. Thus, whereas the esters of a dibasic acid in (on) nitrobenzene behaved normally, the free acids in water did not. Yet in water the acids were horizontally oriented, as judged from film thickness. The difference in behavior is interpreted, again, as due to the lateral attraction of the chains which is nullified in nitrobenzene by the interaction with the solvent but which in water becomes evident when the chains are sufficiently long. Some of the data reported by Taubman are collected in Table I-3. These studies seem to demonstrate a marked effect of the solvent upon the nature of the adsorption.

Lateral attractions between the chains are also manifested by the regular increase in temperature required to bring about a given expansion of the film. Adam[56] utilized the temperature of expansion as a means of comparing lateral attractions between molecules of different lengths and shapes. He defined a temperature of half-expansion as that which at a specified low pressure brought the area of a surface film halfway from that of the condensed film to that of the expanded film. He found

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[56] Adam, *Proc. Roy. Soc. London,* A101, 516 (1922).

TABLE I–3

Comparison of Thickness of Surface Film at Saturation with Minimum Area Occupied by a Molecule of the Substance

Substance[a]	Min. area per mol. in satd. film, A.^{2}	Thickness of film[b] × 10^8 cm.	Substance[c]	Min. area per mol. in satd. film, A.^{2}	Thickness of film × 10^8 cm.
Benzene	37.5	3.9	Glutaric	48.7	(3.8)
Naphthalene	51.5	3.6	Pimelic	56.8	4.6
Cetylbenzene	110.0	5.2	Azelaic	65.8	4.6
Hexane	46.0	4.7	Sebacic	71.3	4.7
Decane	63.4	4.9	Diethyl oxalate	45.9	4.9
Cetene	91.8	5.0	Diethyl malonate	51.5	4.8
Cyclohexane	40.3	4.4	Diethyl sebacate	56.8	4.9
n-Butyl alcohol	24.2	6.2	Decamethylene glycol	69.0	4.7
n-Octyl alcohol	25.4	10.1	Ethylurethan	29.0	4.6
Butyric acid	29.0	5.2	Pyridine	38.5	3.5
Ethyl decanoate	39.2	9.8	α-Picoline	44.6	3.6
Diethyl sebacate	87.0	5.0	β-Picoline	40.2	4.0
			α,α′-Lutidine	48.5	3.8
			Piperidine	26.6	6.1
			Quinoline	30.6	6.4
			Nicotine	51.5	5.2

[a] Nitrobenzene solution–air interface.[55] [b] Calculated from Gibbs' equation for adsorption, using cryoscopically determined activities. [c] Aqueous solution–air interface.[55]

that addition of one CH_2 group to the chain, irrespective of the nature of the polar end group, raised the temperature of half-expansion by about 10° near 0°, and by 7 or 8° near 50°. This does not imply that polar end groups do not contribute to the lateral interactions. They show effects on the rigidity and on other properties of the films. The subject is reviewed by Adam.[57]

3. Liquid–Liquid Interface

The situation at a liquid–liquid interface is much the same as that sketched above for the liquid–vapor interface. The chief difference expected is that if the liquids which compose the interface are quite unalike then added molecules in the interface may be subjected to strong orienting forces. Strong orienting forces may not necessarily imply greater adsorption. For example, Harkins[58] predicted and has shown that the water–water vapor interface should be a better "trap" for polar molecules such as those which have been under discussion than the water–benzene interface, since the discontinuity between the two phases is greater at the former than at the latter interface. He measured the adsorption of butyric acid at the two interfaces and found that when the concentration in the phases was low there was greater adsorption at the former than at the latter interface, but that the same value was approached for both interfaces as the concentration in the phases was increased and as the adsorption increased. This indicated that the area per molecule in tightly packed interfacial monolayers was dependent on geometrical considerations more than on whether the interface was composed of the one or of the other pair of phases.

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[57] N. K. Adam, *The Physics and Chemistry of Surfaces,* 3rd ed., Oxford Univ. Press, London, 1941.

[58] Harkins, in *Surface Chemistry.* Publication No. 21, Am. Assoc. Adv. Sci., Washington, 1943, p. 40.

At a water–paraffin oil interface an adsorbed aliphatic molecule would be expected to be oriented so that the hydrocarbon portion of the chain would be in or near the petroleum phase while the polar group would be in the aqueous phase.[59] A fatty acid salt, with ionic character greater than that of the free acid, would be more soluble in the water phase, but if it had a long hydrocarbon chain it might be expected to be very strongly adsorbed and oriented. (This accounts in part for the remarkable emulsifying properties of this class of compounds.)

If the adsorptive is virtually insoluble in both of the liquid phases ("oil" and "water") so that saturation of both phases is readily reached, then monolayers at this interface can be produced.[60] The technique of measuring the properties of these films is fraught with difficulties. Instead of using a film balance and manipulating the area of the film with barriers[61] it proves much more practical[62] to employ a fixed area and decrease the area available per molecule by adding more molecules in a controlled way to the film. This method was developed by Alexander and Teorell.[62] The film pressure is determined from the difference in interfacial tensions between the original, clean interface and the interface after addition of adsorptive, using a ring method (Chapter II).

These studies[63] have shown that at the liquid–liquid interface many substances (such as proteins) spread more rapidly and completely than at the air interface. At the stage of a tightly packed film the area occupied by the molecules is the same in both kinds of interface. An important feature of these films is that because the hydrocarbon parts of the molecules dissolve in the "oil" layer their mutual interactions may disappear (see Frumkin and Taubman's work, referred to above). The equations for the behavior on compression of surface films at the "oil–water" interface are often simpler than those for the behavior at the air–

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[59] Harkins, Brown, and Davies, *J. Am. Chem. Soc.*, 39, 354 (1917).

[60] Askew and Danielli, *Proc. Roy. Soc. London,* A155, 695 (1936).

[61] Askew and Danielli, ref. 60, and *Trans. Faraday Soc.*, 36, 785 (1940).

[62] A. E. Alexander and Teorell, *Trans. Faraday Soc.*, 35, 727 (1939).

[63] A. E. Alexander, *Repts. Progress Phys.*, 9, 158 (1942–43).

water interface because the term for this mutual interaction may be eliminated.

Boundary potentials,[62,64] interfacial viscosity,[64] and changes in the state of the film have also been measured for these interfaces. Some very large molecules have been spread.[65]

As the two liquid phases that form the interface are made more and more alike they also become more soluble in each other. There is then less of a discontinuity found in the region of the interface and adsorption may be less pronounced. Orientation would be expected to be less marked. Further progress in this direction leads to dissolution of the two liquids, no interface and, hence, no adsorption.

4. Liquid–Solid Interface

It should not be anticipated that the entire molecular picture drawn for vapor–liquid and liquid–liquid interfaces can apply also to liquid–solid interfaces, for these latter differ in many respects from the mobile interfaces. The liquid surface is homogeneous in the directions which make its area (though not homogeneous normal to the surface), the homogeneity being maintained by the thermal shuffling of the molecules. Thus, except for very viscous liquids, and cases bordering between liquid and solid, there will be a uniformity in the liquid surface not usually found with solid surfaces. The likely inhomogeneity of solid surfaces was pointed out earlier but needs more detail here, since organic chemists and others make greatest use for separation purposes of adsorption at liquid–solid interfaces.

One special case of "adsorption" at the liquid–solid interface needs to be mentioned briefly. When crystals grow from solution there is at the surface the laying down of molecules from the solution. This might be construed as an adsorption process, though it is normally not so described. Only if molecules foreign to the crystal are laid down is it spoken of as adsorption. The phenomenon of crystal growth has received a great deal of attention. Discussions of it must be sought elsewhere.[66]

Liquid–solid interfaces may, for the sake of convenience, be classified as follows: solid–pure liquid; solution–plane solid; solution–solid (not plane). In each of these cases subclasses may be distinguished which are characterized by the nature of the solid: whether pure substance, or a mixture; whether crystalline or amorphous. The solutions may contain one, or several, solutes.

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[64] A. E. Alexander, *Trans. Faraday Soc.*, 37, 117 (1941).

[65] Crisp, *J. Colloid Sci.*, 1, 49, 161 (1946).

[66] France, in J. Alexander, *Colloid Chemistry*. Vol. V, Reinhold, New York, 1944, p. 443. See especially Discussion No. 5. "Crystal Growth," *Faraday Soc.*, 1949.

A. SOLID—PURE LIQUID INTERFACE

One of the most important advances in understanding the molecular aspects of adsorption at liquid–solid interfaces has been the demonstration that phase changes, probably similar to those observed for films on liquids, can be found for films on solids.[67] Certain differences are, of course, observed. For example, film pressures are often higher on solid than on liquid surfaces; the phase changes are less sharp and often difficult to discern; the films show a tendency to become more than one molecule thick. The evidence for these phase changes has been summarized,[68] together with methods for recognizing them.[67,69]

If a liquid–pure solid interface is under examination the only way to vary the concentration of the adsorptive is by working with it as a vapor, or as a liquid under pressure. In the first case the interface is vapor–solid for at least part of the isotherm. Harkins and Jura[70] showed that when water is adsorbed on the polar, nonporous, crystalline solid anatase (TiO_2) at 25° the thickness of the film formed increases with the pressure of the water vapor, and as the pressure approaches saturation the film becomes about 15 A. thick. This corresponds to about 5 layers of water molecules, the first layer being somewhat loosely packed. Anatase is well wetted by water. These authors also demonstrated that nitrogen near its saturation pressure at —195.8° attains a film thickness of some 10 molecules, or about 36 A., on this solid. At 0°, butane on this solid yields a film about 64 A. thick near saturation. It appears that in the first layer of this film the butane molecules lie flat on the surface; the outside of the film may be nearly like the surface of liquid butane. There is evidence that the presence of the solid is felt up through the entire film, though to a nearly exponentially decreasing extent toward the outside of the film.

Frazer, Patrick, and Smith[71] prepared a virgin glass surface out of contact with water, and found that on this presumably plane surface toluene showed no evidence of multimolecular adsorption, but after cleaning the surface with cleaning solution and nitric acid, the planar character was destroyed and evidence for multimolecular adsorption of toluene was obtained. Latham[72] investigated the matter further, using in place of toluene the more polar acetonitrile and nitromethane. He found that on fire-polished glass the films obtained were not essentially thicker than one molecule for these polar substances, but that on acid-treated glass, films of about 50 molecules thickness were obtained for both polar and nonpolar substances. A presumably nonpolar surface made by electrolytic deposition of mercury on platinum adsorbed water quite strongly, forming a layer about 30 molecules thick, while a presumably plane surface made by electrolytic amalgamation of a silver surface adsorbed water in a film not over one molecule thick. Earlier work on this subject has been discussed by Cary and Rideal.[73] Fowkes and Harkins[74] found, in the adsorption of butanol, butyric acid, butylamine, sodium butyrate,

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[67] Harkins and Jura, in J. Alexander, *Colloid Chemistry*, Vol. VI, Reinhold, New York, 1946, p. 1; Jura, Loesser, Basford, and Harkins, *J. Chem. Phys.*, **14**, 117 (1946); Jura, Harkins, and Loesser, *ibid.*, **14**, 344 (1946).

[68] Harkins, in Weissberger, *Physical Methods of Organic Chemistry*, 2nd ed., Interscience, New York, 1949, Part I, pp. 427–485.

[69] Gregg and Maggs, *Trans. Faraday Soc.*, **44**, 123 (1948).

[70] Harkins and Jura, *J. Am. Chem. Soc.*, **66**, 919 (1944).

[71] Frazer, Patrick, and Smith, *J. Phys. Chem.*, **31**, 897 (1927).

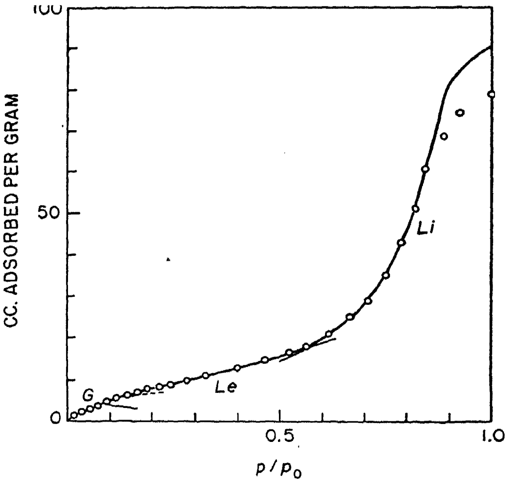

Fig. I-4. Adsorption isotherm showing phase changes in the film in the adsorption of *n*-butane on a porous solid.[75] The phases are designated: *G*, gaseous; *Le*, liquid expanded; *Li*, liquid intermediate. The effect of pores in limiting the amount of material being adsorbed is thought to be shown by the departure of the observed values (○) from the calculated (solid line) at the higher relative pressures. p/p_0 is the relative pressure.

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[72] Latham, *J. Am. Chem. Soc.*, 50, 2987 (1928).

[73] Cary and Rideal, *Proc. Roy Soc. London,* A109, 301 (1925).

[74] Fowkes and Harkins, *J. Am. Chem. Soc.*, 62, 3377 (1940).

propionic or acetic acids from water solutions of concentrations up to 1 molal on to paraffin, stibnite, talc, or graphite, that the film of adsorbed material was unimolecular, but that no complete monolayer was formed in any instance.

If the pure liquid is adsorbed on a porous solid the effects of condensation in capillaries enter the picture. A curve illustrating phase changes in such a case is given by Jura and Harkins[75] (Fig. I-4). In this curve there can be seen two phase changes, and in addition the effect of capillaries, which shows up at the high pressure end of the curve, where the calculated line does not fall on the observed values.

B. SOLUTION—SOLID INTERFACE

The invariable feature of adsorption at the solution–solid interface is the competition[76] which exists there between solvent and solute molecules for the surface. This is discussed in Chapter III.

When a solute is adsorbed on a nonporous crystalline surface from solution it may form a film one molecule in depth, as was mentioned above. Bartell and Benner[77] concluded from studies of adsorption of isoamyl alcohol and cyclohexanol at water–isooctane and silica–isooctane interfaces that the adsorbed film need not be more than one solute molecule thick to account for the data, and that in both cases the alcohol molecules were oriented with the polar group toward the polar phase (water in the former and silica in the latter system). Harkins and Jura[78] showed that when stearic acid was adsorbed from dry benzene on titanium dioxide the film probably was loosely packed because under the conditions of the experiment only about 70% as much stearic acid was adsorbed as that calculated to be required for a close-packed film. Also, Smith and Fuzek[79] studied the adsorption of lauric and palmitic acids from benzene (other acids and other solvents were also used in some experiments) on Raney nickel and Adams' platinum catalyst and concluded that the acids were adsorbed in an oriented, unimolecular layer which made it possible to calculate the specific surface of the catalyst from the amount of fatty acid adsorbed and the cross-sectional area of the fatty acid molecule.

In certain cases of which only a few out of a great many have been given above, the solution–solid interface behaves in what appears to be an uncomplicated manner. However in many other cases the behavior is very complicated, and the molecular aspect often difficult to picture. The over-all behavior is the resultant of the operations of factors arising from the adsorbent, the solution, and the interface.

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[75] Jura and Harkins, *J. Chem. Phys.*, 12, 114 (1944).

[76] Berl and Wachendorff, *Kolloid-Z.*, 36 (Zsigmondy Festschrift), 36 (1925).

[77] Bartell and Benner, *J. Phys. Chem.*, 46, 847 (1942).

[78] Harkins and Jura, *J. Am. Chem. Soc.*, 66, 919 (1944).

[79] H. A. Smith and Fuzek. *J. Am. Chem. Soc.*, 68, 229 (1946).

The *effects of the solid adsorbent* on the adsorption result from its chemical composition and its physical structure. With regard to the chemical composition, little needs to be said beyond a few general statements. Solid adsorbents are usually classed (chemically) as polar and nonpolar. The polar solids are those which interact attractively with molecules through the London dispersion forces and forces due to "segregated" electric charges, and in which the relative intensity of the dispersion interaction is not great compared with the other (dipolar, etc.) type.[80] Polar solids may be crystalline or amorphous. Some few examples are quartz, barium sulfate, titanium dioxide, alumina, silica gel, glass, organic ion-exchange resins, zeolites. In nonpolar solids the interactions due to dispersion forces preponderate over those due to dipoles. Examples of nonpolar solids are certain charcoals (see below), paraffin, graphite, and a number of organic resins and plastics. It is impossible to draw a sharp classification between polar and nonpolar adsorbents; one can correctly speak only of more or less polar adsorbents.

If the solid surface is free from impurities, then its chemical properties may be inferred from the properties of the bulk substance. The surface of the adsorbent may be homogeneous or heterogeneous in nature. It may contain regularly placed functional groups (ions, etc.) which form an orderly pattern over the surface, as found on clean metal surfaces and clean crystalline surfaces. Such surfaces may be homogeneous in one direction and homogeneous but different in structure in another (anisotropic surface).

The surfaces may be heterogeneous, with irregularly arranged functional groups. This may give rise on such adsorbents to "active patches" where adsorptions of special kinds may occur.[81] The chemical nature of the surface may be changed by appropriate treatment, for example, by coating the adsorbent with organic substances,[82] or with metals.[83] It may also be changed by other chemical treatments. For example, the adsorption behavior of charcoal can be altered within wide limits by pretreatment. Bartell and Lloyd[84] showed that by suitable treatment (use of different temperatures and different gases) the surface of a charcoal may be made quite nonpolar, or polar to an extent approaching silica gel, as judged by adsorptive properties. There is a very extensive literature on this subject,[85] and it suggests one reason why it is better to speak of the adsorbent "activated charcoal" rather than "activated carbon," since the latter name may mislead the unwary.

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[80] Harkins and Jura, *J. Am. Chem. Soc.*, **66**, 919 (1944).

[81] H. S. Taylor, *Chem. Revs.*, **9**, 1 (1931).

[82] Acharya, *J. Indian Chem. Soc.*, **13**, 723 (1936); **14**, 188 (1937); **18**, 15 (1941).

[83] Ryerson and Cines, *J. Phys. Chem.*, **46**, 1060 (1942).

[84] Bartell and Lloyd, *J. Am. Chem. Soc.*, **60**, 2120 (1938).

If the surface of an adsorbent contains impurities, these may markedly affect its chemical nature, as the history of catalytic promotors shows, but it is often very difficult to tell whether a given effect is due to impurities or to some special arrangement of the molecules of the adsorbent or to some physical circumstance. For example, Bente and Walton[86] found that only a small percentage of the total surface of a nitrogenous charcoal was responsible for most of the catalytic activity of the surface in influencing the rate of decomposition of hydrogen peroxide, and the oxidation of hydroquinone and of alkaline potassium urate. Heymann and Boye[87] observed that the adsorption of fatty acids on gold powder from water was decreased after boiling the gold with nitric acid, though no gold appeared in the solution and only traces of silver and iron.

A great deal of experimentation and discussion, approached from many points of view, has concerned itself with the physical nature of the surfaces of solid adsorbents. By the surface is meant here the macro- or microscopic surface, not the "surface" at the submicroscopic, or molecular, level where oscillations of individual molecules and such phenomena are apparent.

Smooth surfaces for adsorption studies are difficult to obtain. Frazer, Patrick, and Smith[88] concluded that the use of a supercooled liquid (glass) offered the best possibility of securing a smooth surface. They found the properties of the glass surface markedly different after the surface was "cleaned" with acid (see above). The difficulty of obtaining smooth solid surfaces with metallic properties has led to the use of mercury surfaces.[89] Cold-rolled steel surfaces have been obtained very nearly

[85] Gurvitsch, *J. Russ. Phys. Chem. Soc.*, 47, 805 (1915); Farmer and Firth, *J. Phys. Chem.*, 28, 1136 (1924); Tryhorn and Wyatt, *Trans. Faraday Soc.*, 21, 399 (1925–26); H. S. Taylor, *J. Phys. Chem.*, 30, 145 (1926); Foote and Dixon, *J. Am. Chem. Soc.*, 52, 2170 (1930); Landt and Knop, *Z. Elektrochem.*, 37, 645 (1931); Okrent, *J. Chem. Soc.*, 1932, 613; Frampton and Gortner, *J. Phys. Chem.*, 41, 567 (1937); Emmett, *Chem. Revs.*, 43, 69 (1948).

[86] Bente and Walton, *J. Phys. Chem.*, 47, 133 (1943).

[87] Heymann and Boye, *Z. physik. Chem.*, A150, 219 (1930).

[88] Frazer, Patrick, and H. E. Smith, *J. Phys. Chem.*, 31, 897 (1927).

[89] Cassel and Salditt, *Z. physik. Chem.*, A155, 321 (1931); Cassel, *J. Phys. Chem.*, 8, 195 (1944).

plane,[90] but even polished and annealed surfaces may not be plane.[91] Brown and Uhlig[92] studied the surface area (area accessible to ethane at —183°) of chrome-plated nickel strips before and after etching and found that for three samples before and after etching with hydrochloric acid the ratio of accessible area to apparent area was 15:27, 12:9.4, and 49:53. Surface cracks and fissures, said to be typical of chromium electroplates, were observed in photomicrographs, and also a network of protuberances and deep valleys, which were visible on higher magnification. From this and other similar and related studies[93] it is apparent that the magnitude of the accessible area is affected by the previous history of the surface. It is interesting that areas measured by gas adsorption and those calculated from particle size as determined by the broadening of diffraction bands in x-ray powder diagrams can agree fairly well in certain cases. A discussion of this has been given by Zettlemoyer and Walker[94] with data for magnesia adsorbents.

In the case of crystalline surfaces with faces, corners, and edges in large numbers, it would seem that even though the adsorbent is a single pure substance there will be sites of different kinds where adsorption may occur. In the plane face of a crystal any molecule or ion is surrounded on all sides, except the interfacial side, by other molecules or ions of the substance. Along the edges of the crystal the molecules are more exposed, and hence show more residual attractive forces. At corners of crystals the molecules are most exposed, and so most reactive. One might rank such locations according to the energies of the molecules present:

$$\text{corners} > \text{edges} > \text{faces}$$

This same ranking also holds for the order of melting when the crystal is heated, and for the same physical reasons. The energies of molecules and ions at different locations in the surfaces of crystals have been calculated and discussed by Lennard-Jones and Taylor[95] and by Stranski[96] and others.

With porous adsorbents the picture becomes even more complicated. Charcoal has been a much used adsorbent. A good many of the studies of porous adsorbents have been concerned with the "reversal of Traube's rule" shown in some adsorptions. According to this rule (see above) adsorption at the water surface should increase regularly for the members of a homologous series with increase in number of CH_2 groups in the chain. When this rule was extended to adsorption at the water–charcoal interface it was found that adsorption on some charcoals followed the rule; on others the rule was not followed, or was reversed.[97] This is a matter of some practical importance when the adsorbent is used for separating mixtures of homologs. Herbst[98] argued that the adsorption performance of a charcoal does not go proportionally to the surface area. It depends much more on the number of active, freely accessible and "not saturated" carbon molecules present. The activity is not the property of a surface, he said, but the property of a spatial structure, namely, of the active carbon molecules. Porosity makes these accessible.[99] He stated further that to test the "true activity" of a charcoal[100] one should use the smallest molecule possible, *i.e.*, hydrogen. With a series of larger molecules such as He, N_2, O_2, A, CO, CO_2, NH_3, SO_2, CH_3Br, etc. one gets an "ultraporosity decrease" in the adsorption, since the larger molecules cannot enter the smaller capillaries.[101] This kind of argument underlies the necessity for operational definitions of "surface area," "surface activity," and such (Chapters II and IV).

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[90] Armbruster, *J. Am. Chem. Soc.*, **68**, 1342 (1946).

[91] Bowden and Rideal, *Proc. Roy Soc. London,* **A120**, 59, 80 (1938).

[92] Brown and Uhlig, *J. Am. Chem. Soc.*, **69**, 462 (1947).

[93] Burwell, Smudski, and May, *J. Am. Chem. Soc.*, **69**, 1525 (1947).

[94] Zettlemoyer and Walker, *J. Phys. & Colloid Chem.*, **51**, 763 (1947).

[95] Lennard-Jones and P. A. Taylor, *Proc. Roy. Soc. London,* **A109**, 476, 501 (1925).

[96] Stranski, *Z. physik. Chem.*, **136**, 259 (1928); but see Bunn and H. Emmett, in Discussion No. 5, *Faraday Soc.*, 1949, p. 119 *ff.*, and Bunn, *loc. cit.*, page 132 *ff.*

Bruns[102] prepared a sugar charcoal by coking sugar and activating it at 1000° in the presence of hydrogen. He studied the effect of reduction of particle size of the adsorbent on the adsorption from 0.01 *N* solution in water of the fatty acids from 1 to 6 carbon atoms in chain length. Upon reduction in size of the charcoal particles the adsorption of the higher members of the fatty acid series increased more than that of the lower members. Because of this Bruns was able, from a charcoal which showed reversal of Traube's rule, to obtain through reduction in particle size a charcoal which followed Traube's rule. According to Bruns this behavior showed that the reversal of Traube's rule is due to the presence of pores, which are not accessible to molecules with large volume, and which are opened by mechanical partical-size reduction of the charcoal. This supported the "ultraporosity theory" of the cause of reversal of Traube's rule. In evaluating this work it should be noted that the adsorption was carried out at a single initial concentration, and that the charcoal had not been activated in an oxidizing atmosphere.

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[97] Nekrassow, *Z. physik. Chem.*, **136**, 18, 379 (1928); Miller, *Colloid Symposium Monograph*, **5**, 55 (1928); Sabalitschka, *Pharm. Ztg.*, **74**, 382 (1929); Landt and Bhargava, *Z. Ver. deut. Zuckerind.*, **79**, 470 (1929); Dubinin, *Z. physik. Chem.*, **150**, 145 (1930); **155**, 116 (1931); Bruns, *Kolloid-Z.*, **54**, 33 (1931); Landt and Knop, *Z. Elektrochem.*, **37**, 645 (1931); Iliin, *Z. physik. Chem.*, **A155**, 403 (1931); Krczil, *Kolloid-Z.*, **58**, 68 (1932); Heymann and Boye, *ibid.*, **63**, 154 (1933).

[98] Herbst, *Kolloid-Z.*, **38**, 314 (1926).

[99] Herbst, *Biochem. Z.*, **115**, 204 (1921); *Kolloidchem. Beihefte*, **21**, 1 (1925).

[100] Herbst, *Biochem. Z.*, **118**, 103 (1921).

[101] Emmett, *Chem. Revs.*, **43**, 69 (1948).

[102] Bruns, *Kolloid-Z.*, **54**, 33 (1931).

On the other hand, Krczil[103] found that there was no increase in adsorptive power over the starting material when de-ashed sugar charcoal of particle size 0.2 to 0.1 mm. was reduced to particle sizes less than 0.05 mm. The adsorption was tested on fatty acids from their 0.01 *N* aqueous solution. There were evident some differences in behavior with different methods of activation, and so the reversal of Traube's rule with change in particle size observed by others must, he felt, be laid to some factors already present in the charcoal due to its pretreatment. Linner and Gortner have illustrated the danger of drawing conclusions from adsorption comparisons made at a single initial concentration.[104]

Dubinin[105] had at one time postulated that the reversal of Traube's rule might be explained by the conversion of the sugar charcoal surface to a crystalline structure (x-ray evidence) under the influence of temperatures above 700°. However, he later gave up this working hypothesis when he demonstrated that finely crystalline charcoals made by other methods gave adsorptions which followed Traube's rule. Also, surface oxides produced on charcoals (see below) could not account for the reversal. The best explanation of his results[106] was made on the ultraporosity theory. This theory was analyzed by Ockrent,[107] using data obtained from the adsorption isotherms of a number of fatty acids, aromatic acids, and chlorinated acetic acids on ash-free sugar charcoal.[108] From the adsorption of salicylic acid it was calculated that there were 4 molecules adsorbed for each 92 carbon atoms in the bulk adsorbent. Assuming the carbon atoms to be 1.5 A. apart and the salicylic molecule to occupy an area of some 24 A.^{2}, he concluded that the particles of charcoal must be largely assemblies of ultrapores. He concluded that small molecules would be able to penetrate fine pores which might be inaccessible to large molecules, and that if the pores tapered or were otherwise irregular the smaller molecules might be able to penetrate more deeply. Grinding of these particles might then increase the surface available to large molecules and perhaps decrease it for smaller ones, for the area available to all molecules would be increased by increasing the number of particles; but by blocking up some of the ultrapores with colloidal particles a decrease in surface felt mostly by the smaller molecules would result. However, the area at the mouths of the ultrapores might be increased by the surface of the blocking colloidal particles, an increase in area which would affect all molecules. If such charcoals were then activated in oxygen all the particles would be partly consumed, and for a given weight of charcoal there would be more particles and hence more surface available to all molecules. However, any burning off of the colloidal particles clogging the ultrapores would cause a greater relative increase in area for the smaller molecules.

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[103] Krczil, *Kolloid-Z.*, 58, 68 (1932).
[104] Linner and Gortner, *J. Phys. Chem.*, 39, 35 (1935).
[105] Dubinin, *Z. physik. Chem.*, 140, 81 (1929).
[106] Dubinin, *Z. physik. Chem.*, 150, 145 (1930).
[107] Ockrent, *J. Chem. Soc.*, 1932, 1864.
[108] Ockrent, *J. Chem. Soc.*, 1932, 613.

That other variables may exist in these systems is to be concluded from the following considerations. The rate at which equilibrium is established may vary considerably with chain length. Baum and Broda[109] studied the adsorption of acetylated carbohydrates of different viscosities (different molecular weights) on alumina and charcoal. Equilibrium was not established even after several months. The establishment of adsorption equilibrium required less time for shorter chain compounds (which diffused more rapidly) than for long-chain compounds. It was concluded that the slow adsorption of the long-chain compounds might well cancel the effect of their greater adsorbability if equilibrium were not reached. The equilibrium adsorbability increased with chain length; the rate of approach to equilibrium decreased. This is admittedly an extreme case, but Iliin and Kiselev[110] found that the time required for fatty acids and iodine to reach adsorption equilibrium on wood charcoal decreased with grain size of the charcoal. Thus it would be important to ensure the attainment of equilibrium in experiments investigating the effects of pore size. This subject has been discussed for gas adsorption by Gleysteen and Deitz.[111]

In this connection also, it is interesting to recall experiments by Bikerman[112] in which he deposited monolayers of higher fatty acid on a grooved slide. He found a deposition ratio of 0.98 where the deposition ratio is area of monolayer deposited/geometrical area of the plate. In this case the geometrical area did not take into account the grooves. On wire gauze an average deposition ratio of 0.86 was obtained. This seemed to indicate that at the moment of deposition the monolayers are like soap films stretched between the irregularities of the surface.[113] These films probably burst soon after their preparation. One can imagine, however, that rough places on adsorbents, and the mouths of ultrapores might in some instances be bridged over by laterally adhesive adsorptive molecules. This effect would not be observed if the lateral adhesion were cancelled by interactions with the solvent such as those found to occur at "oil–water" interfaces (see above, and Chapter II).

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[109] Baum and Broda, *Trans. Faraday Soc.*, **34**, 797 (1938).

[110] Iliin and Kiselev, *Kolloid-Z.*, **66**, 28 (1934); see also Dubinin, *Z. physik. Chem.*, **155**, 116 (1931).

[111] Gleysteen and Deitz, *J. Research Natl. Bur. Standards*, **35**, 285 (1945).

[112] Bikerman, *Proc. Roy. Soc. London*, **A170**, 130 (1939).

The reversal of Traube's rule, which has been used to provide some evidence about the nature of charcoal surfaces, was observed by Holmes and McKelvey[114] for adsorption of fatty acid on a silica gel from toluene. These authors laid the reversal to competition between the very polar silica gel surface and the nonpolar solvent for the fatty acids. The lower fatty acids, being more polar in nature than the higher, were more strongly adsorbed. The order of increasing adsorption of the acids from toluene was:

$$\text{caprylic} < \text{butyric} < \text{propionic} < \text{acetic} \quad .$$

Cassidy[115] showed that the extent of adsorption of lauric, myristic, palmitic, and stearic acids from petroleum ether onto several commerical charcoals increased in that order. The order was reversed for several other commercial charcoals and for silica gel. Alumina showed no distinction between the acids. Several charcoals gave curves which crossed each other, so that the order at a lower concentration was different from that at a higher one.

These data emphasize that no single feature of an adsorbent surface can be called upon to explain the different types of adsorption behavior observed. Also, since adsorption curves of homologous compounds may cross each other, a ranking of relative adsorbabilities taken at just one concentration may be quite different from one taken at another concentration.[116]

The factors which affect the molecular aspect of the adsorption *from the side of the solution* may be discussed under four headings: the competitions which occur between solute and solvent for the surface; the dissociations which may occur in the solution, thus introducing additional molecular species; the exchange of ions or molecules with the adsorbent; and the influence on the rate of attaining equilibrium. Of these, the most important, because ubiquitous, is the first.

[113] Bikerman, *Trans. Faraday Soc.*, 34, 800 (1938).

[114] Holmes and McKelvey, *J. Phys. Chem.*, 32, 1522 (1928).

[115] Cassidy, *J. Am. Chem. Soc.*, 62, 3073 (1940).

[116] Linner and Gortner, *J. Phys. Chem.*, 39, 35 (1935).

Whenever a solid adsorbent is introduced into a solution the components of the solution will *compete for the interface.* Williams[117] was apparently one of the first to call attention clearly to the role played by adsorption of solvent. He said: "The tendency has been to regard the solvent as a 'space' in which the solute has play," and he pointed out that this introduced errors in adsorption calculations in which the adsorption of solvent was not evaluated. These errors were small with dilute solutions, but became important with increase in concentration of solute. Later studies with other adsorbents and mixtures[118] showed that at the ends of the concentration ranges the component present in smaller amount was usually preferentially adsorbed (Chapter III).

With binary and multicomponent mixtures it sometimes is difficult to be satisfied that the adsorption results are due to a simple competition between the components for the surface of the adsorbent; in other cases the conclusion seems justified. A few examples from a voluminous literature will suffice to make this point.

If a simple competition were involved, then increase in the concentration of one solute should produce a decrease in the adsorption of the other. This sequence of events has been observed in many experiments. The early work has been reviewed by Freundlich.[119] Ockrent[120] investigated the adsorption of fatty acids, aromatic acids, and chlorinated acetic acids from water onto practically ash-free sugar charcoal. From calculations based on the Langmuir isotherm he concluded that the available area on the adsorbent was the same for all acids. A similar conclusion was reached by Caliri[121] for mixed organic acids from water onto medicinal charcoal, and by Yermolenko and Levina[122] for adsorption of salicylic or butyric acids from mixed solvents on animal charcoal. Using the char-

[117] Williams, *Medd. Vetenskapsakad. Nobelinst.*, 2, No. 27 (1913).

[118] Williams, *Trans. Faraday Soc.*, 10, 155 (1914); Wo. Ostwald and Izaguirre, *Kolloid-Z.*, 30, 279 (1922); Wo. Ostwald and Schulze, *ibid.*, 36, 289 (1925); Patrick and D. C. Jones, *J. Phys. Chem.*, 29, 1 (1925); Heymann and Boye, *Kolloid-Z.*, 63, 154 (1933); Bartell and Sloan, *J. Am. Chem. Soc.*, 51, 1643 (1929); Bartell, Scheffler, and Sloan, *ibid.*, 53, 2501 (1931); Bartell and Scheffler, *ibid.*, 53, 2507 (1931); Jones and Outridge, *J. Chem. Soc.*, 1930, 1574; M. R. A. Rao, *J. Indian Chem. Soc.*, 12, 345, 371 (1935); K. S. G. Doss and B. S. Rao, *Half-yearly J. Mysore Univ.*, 8, 49 (1935–36); K. S. Rao and B. S. Rao, *Proc. Indian Acad. Sci.*, A4, 562 (1936); Venkatanarasimhachar and K. S. G. Doss, *ibid.*, A6, 32 (1937); Bartell and Lloyd, *J. Am. Chem. Soc.*, 60, 2120 (1938); N. S. Rao and Jatkar, *Quart J. Indian Inst. Sci.*, 5, 72, 80, 87, 91, 98 (1942).

[119] H. Freundlich, *Colloid and Capillary Chemistry*. Methuen, London, 1926, p. 199 *et seq.*

[120] Ockrent, *J. Chem. Soc.*, 1932, 613.

[121] Caliri, *Dissertation*, Fribourg, 1940.

[122] Yermolenko and Levina, *Acta Physicochim., U. R. S. S.*, 10, 451 (1939).

coal Darco G-60, Hagdahl and Holman[123] were able to separate homologous fatty acids by displacement development, using a higher acid as displacer. This showed that the fatty acids were adsorbed on essentially the same sites in the adsorbent.

If two substances in a mixture appear to be *adsorbed independently of the presence of each other,* this may be due to their being adsorbed at different sites on the surface.[124] Claesson[125] found that on a number of adsorbents which he examined it was impossible to separate mixtures of fatty acids quantitatively by displacement development. This seemed to argue that the fatty acids were adsorbed independently of each other.

Sometimes the adsorption of one substance is not influenced by the presence of another because the second is not appreciably adsorbed. Weigner, Magasanik, and Virtanen[126] found that the adsorption of sugar on blood charcoal was not recognizably affected by the presence of sodium chloride (2 N) in the solution, nor was the rise in surface tension of the solution caused by the sugar affected. The alkali salts are not very strongly adsorbed. Rona and Toth[127] had found that the adsorption of sugar was decreased in the presence of HCl.

Competitions may show up in comparing the effects of an added component on the adsorptions of homologous substances. Landt and Knop[128] found that the adsorption on ash-free charcoal of dibasic acids from water was affected by mineral acid. The adsorptions of oxalic and malonic acids were less from water than from 0.02 N HCl; but of succinic, glutaric, and adipic the adsorptions were greater from water than from 0.02 N HCl. The effects were not very marked. These investigators found that the fatty acids from acetic through caproic were less well adsorbed from 0.02 N HCl than from water, and that the effect of the mineral acid was less on valeric than on acetic. This may have been due to a competition effect. Adsorption is often, but not always, proportional to the amount of undissociated molecules, experiments having been made with acids[129] and with bases.[130]

The strengthening of adsorption by addition of another solute has been observed. In many cases this can be laid to an effect of the added substance, say a strong electrolyte, in tying up the solvent molecules, say water, so that as a result of the solvation the effective concentration of the adsorbtive is increased. Weigner, Magasanik, and Virtanen[131] found that the adsorption of fatty acids on charcoal was increased by the presence of sodium chloride ($2N$) and that the effect on homologous acids (acetic, propionic, butyric) increased, being least with acetic and greatest with butyric. The effect was also felt in the same sense in the surface tension lowering by the acids. They found, moreover, that the effectiveness of monovalent cations in increasing the adsorption was greatest for lithium and fell from sodium to potassium to ammonium. The order of effectiveness with divalent cations was not clear. The effectiveness increased with the concentration of the salt. Not only the adsorption of fatty acids from water, but also that of ethanol and of acetone was increased by the presence of salt. These authors point out that in many respects this effect on adsorption is related to the anomalies in osmotic behavior produced by salts, the order of increasing anomalous behavior being Cs, Rb, K, NH_4, and Li. This is also the order of increasing hydration of the ions. Analogies are also shown to the influences of neutral salts on the shifts of partition ratios of fatty acids in distillation from aqueous solutions.

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[123] Hagdahl and Holman, *J. Am. Chem. Soc.,* 72, 701 (1950).

[124] Taylor, H. S., *J. Phys. Chem.,* 30, 145 (1926).

[125] Claesson, *Arkiv Kemi. Mineral. Geol.,* A23, No. 1 (1946).

[126] Weigner, Magasanik, and Virtanen, *Kolloid-Z.,* 28, 51 (1921).

[127] Rona and Toth, *Biochem. Z.,* 64, 288 (1914).

[128] Landt and Knop, *Z. physik. Chem.,* A162, 331 (1932) (this paper contains a review).

[129] Phelps and Peters, *Proc. Roy Soc. London,* A124, 554 (1929); Lottermoser and Winter, *Kolloid-Z.,* 66, 276 (1934).

[130] Phelps, *Proc. Roy. Soc. London,* A133, 155 (1931); Rehbinder, *Z. physik. Chem.,* 111, 447 (1924).

These displacement effects are of some interest to chromatography, as shown by the observations of Strain.[132] At an intermediate concentration of alcohol in petroleum ether containing about 5% acetone, fucoxanthin and chlorophyll *a* are difficultly separable on Celite. With less alcohol (about 0.5%) fucoxanthin forms a zone above the chlorophyll; with more alcohol (about 2%) the fucoxanthin zone is below the chlorophyll. With as little as 0.05% amyl alcohol in petroleum ether fucoxanthin is adsorbed above chorophyll *a* on sugar, while with pure petroleum ether it is adsorbed below chorophyll *a*.

The factors *operating within the interface* to influence the molecular aspect of the adsorption can be either chemical or physical. The surface area being limited, it would be expected that the adsorption of one molecule would necessitate the nonadsorption of another unless entirely different sites were involved. But a one-to-one displacement would not necessarily be found. Broda and Mark[133] have visualized the adsorption of a long-chain polymer as consisting of attachment to the surface at many points along the chain, each attachment resulting in the displacement of a solvent molecule. The displacement of many molecules of solvent (say) by one of adsorptive may be brought about also if the adsorptive molecule in occupying a given site blocks, without utilizing, neighboring sites; or if a larger molecule adsorbed at the mouth of a capillary blocks the ingress of smaller molecules.

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[131] Weigner, Magasanik, and Virtanen, *Kolloid-Z.*, 28, 51 (1921).

[132] Strain, *Ind. Eng. Chem., Anal. Ed.*, 18, 605 (1946).

[133] Broda and Mark, *Z. physik. Chem.*, A180, 392 (1937).

Lateral attractive interactions between adsorbed molecules may influence the adsorption and help bring about condensations on the surface.[134] These and other interactions may account for the high densities of some adsorbed films.[135] Ewing and Spurway[136] measured the density of water adsorbed on silica gel at 25.02°, using a gas dilatometer with helium as the inactive gas, and found indications that for small quantities of water, up to about 4.36%, the density of the water on the gel was greater than that of the bulk water at the same temperature by an amount such as would be produced by a pressure of 750 atm. Culbertson and Weber[137] have given evidence that, for samples with large surface, significant errors can arise in density determinations due to a compression of the immersion liquid at the interface.

Molecules in the interface may have considerable freedom to migrate over the surface.[138] Hill[139] believes that localized physical adsorption may be rare at ordinary temperatures. It seems, however, that the existence of immobile layers at some solid–liquid interfaces has been fairly well demonstrated.[140] Bikerman suggests that the immobility may be due to roughness of the surface of the solid. The effects of adsorbable substances on the tensile strengths of solids have been reported by Adam.[141] Apparently, adsorbed films can penetrate surface cracks and wedge them open, thus weakening the solid.

Chemical effects at the interface are observed in ion exchange reactions, and other exchange reactions. These are dealt with in Chapters VII and VIII. Sometimes a given group on a molecule may enhance an adsorption not necessarily because it is the point of attachment but because it influences the rest of the molecule. The effects of halogenation on the strengths of acids illustrates such an influence, and the effect of nitration on the dissociation of phenols.

The molecular picture at the interface would not be complete without mention of the destruction of substances or alterations which can occur in interfaces. Korr[142] has reviewed some of these of biological interest. As an example of a reversible alteration may be mentioned the change in color shown by certain indicators when the water solution is shaken with benzene.[143] The color change appears to take place at the aqueous solution – benzene interface. If the two solutions are separated the original color is restored. Hedvall and Nord[144] found a marked difference in the adsorption of phenolphthalein by black and red mercuric sulfides under the influence of light. Illumination did not affect the adsorption by the black mercuric sulfide, but the red, on illumination, adsorbed up to six times as much phenolphthalein as it did in the dark. The influence of mobile electrons in a surface is discussed by these investigators.

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[134] Cassel, *J. Chem. Phys.*, 12, 115 (1944); Milligan and Rachford, *J. Am. Chem. Soc.*, 70, 2922 (1948).

[135] Lamb and Coolidge, *J. Am. Chem. Soc.*, 42, 1146 (1920); Patrick and Grimm, *ibid.*, 43, 2144 (1921).

[136] Ewing and Spurway, *J. Am. Chem. Soc.*, 52, 4635 (1930).

[137] Culbertson and Weber, *J. Am. Chem. Soc.*, 60, 2695 (1938).

[138] R. M. Barrer, *Diffusion in and through Solids*. Cambridge Univ. Press, London, 1941.

[139] T. L. Hill, *J. Chem. Phys.*, 14, 441 (1946).

[140] Stern, *Z. Elektrochem.*, 30, 508 (1924); Eversole and Lahr, *J. Chem. Phys.*, 9, 530 (1941); Bikerman, *ibid.*, 9, 880 (1941).

[141] Adam, *Nature*, 156, 284 (1945).

5. Interfaces between Three Phases

Three phases may meet to form an essentially linear interface. Such interfaces are encountered at the lines of contact of drops resting on solid or liquid surfaces in a gas or vapor atmosphere, or of drops or bubbles in liquids resting against a solid or liquid surface. At the grain boundaries in metal surfaces exposed to vapors or liquids such interfaces are also expected to occur. There is a large literature dealing with the phenomena associated with these interfaces[145] but very little appears to be known about the molecular structure within the "linear" region.

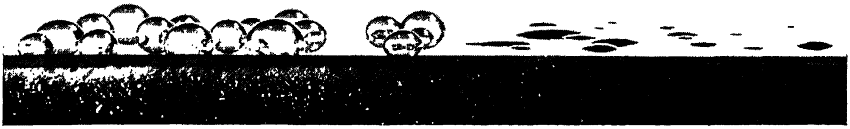

Fig. I-5. At the left are globules of water standing on a waxed glass pane. The edge of the pane is visible across the lower part of the photograph. At the right, on the same surface, are drops of water to which a wetting agent has been added. The water has spread into lenses. (Courtesy Atlas Powder Company.)

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[142] Korr, *Cold Spring Harbor Symposia Quant. Biol.*, 7, 74 (1939).

[143] Deutsch, *Z. physik. Chem.*, 136, 353 (1928).

[144] Hedvall and Nord, *Z. Elektrochem.*, 49, 467 (1943).

[145] J. J. Bikerman, *Surface Chemistry for Industrial Research*, Academic Press, New York, 1947; Harkins, in J. Alexander, *Colloid Chemistry*, Vol. V, Reinhold, New York, 1944, p. 12 *et seq.*; Harkins and Jura, *loc. cit.*, Vol. VI, 1946, p. 1; N. K. Adam, *The Physics and Chemistry of Surfaces*, 3rd ed., Oxford Univ. Press, London, 1941; A. M. Schwartz and J. W. Perry, *Surface Active Agents*, Interscience, New York, 1949.

In three-phase systems the contact angle is one of the most important properties. It is the angle, measured in the liquid, made by the edge of the liquid at the linear interface. It may vary from zero, obtained when the liquid spreads out on the other phase, to nearly 180° (Fig. I-5).

It is apparent that the forces which tend to hold the liquid in the form of a drop (minimum surface area for a given volume) are the forces between the molecules of the liquid—such as are manifested in the surface tension of the liquid. If no other forces were present the liquid would remain a sphere, as it does when falling freely. However, when the drop rests upon a solid surface other forces come into play: there is the force of gravity, which tends to flatten the drop and increase its surface area, thus working against the surface tension. This effect is used to measure surface tension. There is also the interaction of the molecules of the drop liquid with the surface molecules of the solid. If there were no interaction between the molecules of the solid and the liquid, a condition which seems hardly realizable, then this component would be zero, and if the drop were a small one, so that the gravitational effect would be small compared with the surface tension, then one might expect the droplet to exhibit a contact angle of 180°. Because of the operation of one or both of the above effects, observed angles are less than this.

If the interaction between the solid and liquid is negligible, then the contact angle will be greater than 90°, and if the drop is large, so that the surface tension cannot maintain the drop as a sphere, then it will lie on the surface as a flattened sphere. In this case the liquid does not wet the surface. If, on the other hand, there is an interaction between the solid and the liquid, due to the chemical or electrical properties of each, then the liquid will be observed to spread to some extent upon the solid so that its contact angle will have a very small value, becoming zero in the limit, when the drop spreads to a film. Such a liquid wets the surface (Fig. I-5).

The observation of the contact angle is not limited to drops alone, but is possible wherever an interface has an edge. The contact angle of a liquid in a tube or capillary is observable at the edge of the meniscus and it is a common observation that aqueous liquids on clean glass give a very small contact angle (usually approaching zero), whereas the angle between glass and mercury is closer to 180°. In the molecular interpretation of the contact angle as measured for a given system it is essential that the composition of the phases involved be taken into account. The subject is a complex one and cannot be dealt with here.[146]

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[146] A. E. Alexander and P. Johnson, *Colloid Science*, Oxford Univ. Press, London, 1949; A. M. Schwartz and J. W. Perry, *Surface Active Agents*, Interscience, New York, 1949.

IV. SUMMARY

A general description of the factors that may be involved in the simple adsorption of a substance *A* from a solution with *B* onto a solid surface is given to serve as a partial summary of this chapter. The factors operating (1) from the solution side of the interface, (2) from the adsorbent side, and (3) within the interface, have to be considered. In each case the direction of influence of the factor, toward or against adsorption, is weighed.

1. (A) When a molecule is adsorbed from a solution it moves out of a three-dimensional region into a two-dimensional one with attendant restrictions to its freedom. According to the calculations of Broda and Mark[147] and following the statement of Baum and Broda[148] the degrees of freedom corresponding to vibration of the adsorbed molecules "are partly frozen, and do not contribute fully to the phase volume." Other things being equal, the state in which a greater number of degrees of freedom are active is the more probable. Accordingly, this factor, operating from the side of the solution, so to speak, works against adsorption.

(B) If there are any interactions between the molecules of *A* and *B* that tend to cause them to adhere; if there are any hydration effects; or, in general, solvation effects, where the term is used loosely and does not imply any special theory; then such effects would tend to hold the molecules of *A* in solution with *B*. Such interactions would operate against the escape of the molecules from solution whether into the vapor phase or into the interface. Such forces would produce abnormally great solubilities and negative deviations from Raoult's law. They would decrease adsorption.[149]

(C) If the molecules of *A* are not very compatible with those of *B*; if, for example, they tend to associate; or if *B* itself tends to associate and exclude *A*, then such behavior might make *A* less soluble in *B* than expected. This would lead to positive deviations from Raoult's law, and would, in effect, tend to "squeeze" the one molecule out of solution and into the interface. Such effects would tend to increase adsorption.[149]

(D) The kinetic motion of molecules that operates toward making a solution homogeneous would bring molecules into and out of the interface. If no adsorption of *A* occurred there would still be molecules of *A* in the interface, and on the average there would be just as many there as in an equal area taken anywhere in the bulk liquid. But if such a plane in the liquid, of unit area, is compared with unit area of the interface it can be seen immediately that, whereas molecules can diffuse freely through such a plane in the bulk liquid, they have to change the direction of their motion when they enter such a plane in the interface. Adsorption, as Langmuir pointed out,[150] occurs when the molecule that enters the surface dwells there for even a short time. The fact that simple adsorption decreases with increase in temperature is compatible with the above observations: deviations from Raoult's law tend to become less, for a given system, with increase in temperature. The kinetic movement of the molecules, then, brings molecules to the interface and removes them; it neither increases nor decreases adsorption.

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[147] Broda and Mark, *Z. physik. Chem.*, A180, 392 (1937).

[148] Baum and Broda, *Trans. Faraday Soc.*, 34, 797 (1938).

[149] J. H. Hildebrand, *Solubility of Non-Electrolytes*. Reinhold, New York, 1936.

(E) If molecules of A dissociate in solution to form ions (as may a salt) or free radicals (as may many organic compounds, such as hexaphenylethane) or two or more molecules (as may some of the hydrocarbon picrates), then the behavior may lead either to decreased or to increased adsorption. There is evidence, for example, that nonionized molecules of fatty acid are much more effective in lowering the surface tension at the air–solution interface than are ionized molecules[151] (the acids were compared with their salts at equivalent concentrations). Here increased dissociation brought about by some means would decrease the adsorption, whereas decreased dissociation would bring about a condition favorable to adsorption. On the other hand many highly ionized yet very surface active substances are known. This subject is discussed in Chapter III.

2. From the adsorbent side of the interface the forces which might influence the adsorption per unit area of interface are possibly quite numerous.

(A) The chemical nature of the adsorbent may tend to increase adsorption, or actively to oppose it, depending on the chemical nature of the adsorptive and the temperature.

(*1*) If the surface of the adsorbent consists of dipolar molecules and the molecules of A also contain dipoles, then the molecules may be free to equilibrate themselves about a position in which their dipoles are opposed (as regards sign) to those of the adsorbent. There exists then between them an attractive force (coulomb force). Such an interaction would favor adsorption.[152] It would be opposed by increase in temperature for this would increase the motion of the molecules and decrease the period of favorable orientation.

(*2*) If the surface of the adsorbent contains permanent dipoles and the molecules of A are polarizable, then an interaction may occur in which, on the approach of an A molecule to the surface in the proper manner, a dipole is induced in A by the dipole present in the adsorbent. This type of interaction favors adsorption.[152] A corollary of this would be the case in which A contains a permanent dipole and the adsorbent molecules are polarizable. This interaction decreases with increase in temperature.

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[150] Langmuir, *J. Am. Chem. Soc.*, 40, 1361 (1918).

[151] Lottermoser and Winter, *Kolloid-Z.*, 66, 276 (1934).

[152] Magnus, *Z. physik. Chem.*, A142, 401 (1929); Arnold, *J. Am. Chem. Soc.*, 61, 1611 (1939).

(*3*) If any two molecules approach each other, there comes into importance within certain distances the attractive interaction, which is designated by London as the dispersion force. The motion of the electrons in one of these molecules modifies that of the electrons in the other, so that they tend on the average to move in phase.[153] This produces an attractive force proportional to the inverse seventh power of the distance between the molecules. It has been suggested that this force may be an agent in the process of adsorption. This interaction is additive, and of sufficient influence to account in part for the cohesive forces in liquids. The more unlike the molecules that are involved in this interaction the less likely are their electrons to move in phase. This may account for the "squeezing out"[149] action of liquids for small amounts of second substances. If the dispersion forces were responsible for the "structure" found in a liquid then the exclusion of impurities which would distort this structure would be easily pictured. In any case, dispersion forces between adsorptive and adsorbent favor adsorption.

(*4*) If molecules are brought very close together a powerful repulsive force manifests itself, increasing in magnitude enormously as the distance between the molecules becomes very small. This force prevents deep interpenetration of the electron shells of the atoms constituting the two molecules. It comes into importance in adsorption if, for example, a molecule approaches a surface with so much momentum that it overshoots the region of balance between repulsive and attractive forces within which it might oscillate in stable attachment, penetrates closer to the surface atoms, and is repelled so as to overshoot this region and thus not be adsorbed.

(B) The physical composition of the surface may be expected to play a role in the adsorption.

(*1*) On a plane, crystalline, chemically homogeneous surface the disposal of sites at which adsorption can occur will, as Langmuir has pointed out, be in a regular pattern. On an amorphous surface a certain regularity may or may not still be present. The spaces available on a plane crystal surface may be of several kinds, but the regularity of the surface may lead to some sort of stoichiometric relation in the adsorption of different substances.[150]

(*2*) At edges and corners of the adsorbent certain molecules will be in a somewhat exposed condition—perhaps in a strongly curved region of the surface—which may leave them with more capability for interaction than their less exposed neighbors. Such molecules might be more active in adsorbing others, since the lowering of free energy that would occur in the process would be greater for them than for their neighbors.[154]

(*3*) If the surface were rough, then more of the surface molecules would be in an exposed condition, such as that described above, and the roughness might be conducive to an increase in adsorption of small molecules per unit number of surface molecules over the plane surface. But with large molecules the effect might be of the opposite kind. Bikerman's work suggests various possibilities in this connection.[155]

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[153] Lennard-Jones, *Proc. Phys. Soc. London,* **43**, 461 (1931).

[154] Fricke, Blaschke, and C. Schmitt, *Ber.,* **71**, 1738 (1938).

[155] Bikerman, *Trans. Faraday Soc.,* **34**, 800 (1938); *J. Chem. Phys.,* **9**, 880 (1941).

The concept of active centers which has received a great deal of experimental support has originated from considerations of these kinds.

(*4*) If the surface contains capillaries and fissures, then the adsorption may be favored for small molecules that can enter the capillaries, for here they would tend to condense under the pressure of the doubled attraction of two nearby walls (for example) or under the pressure of a curved meniscus.[156] Thus "bulk liquid" might well be formed in these pores or fissures. Larger molecules might be unable to enter the capillaries and thus have, because of their size, considerable adsorption surface excluded to them.

(*5*) If the surface is not homogeneous then the resultant effects can be very complicated indeed. They will not be dealt with here, but may be found discussed in books on catalysis.[157]

3. In the region of the interface itself a number of factors may play a role in adsorption.

(A) An important factor must be the competition between molecules of *A* and *B* for the interface. This occurs because the interface is limited in extent, and nonexpandable (in the cases under discussion) and so differs very much from the bulk liquid phase. More molecules of *A* added to the liquid may increase its volume (of course they may not, if interactions occur that lead to no change—or even contraction—in volume) or at least present the opportunity for increase in volume, while molecules of *A* introduced into the interface generally displace other *A* molecules or molecules of *B*. The adsorption will favor that molecule the adsorption of which occurs with the greater molecular decrease in free interfacial energy, other things being equal.

(B) The area occupied by the molecules in the interface will play a role in the adsorption because a molecule that covers many active spots, for example, a chain molecule, will (other things being equal) be more adsorbable than the monomer. This is because the tendency of molecules to remain in the desorbed state (see above) diminishes with increasing chain length.[158] Here, also, not only size, but shape plays a role.

(*1*) A large molecule may displace several small ones; or a large molecule may block off, without occupying, several sites where adsorption might otherwise occur. The adsorption of small molecules may not be appreciably affected by the presence of large ones if the small can reach areas of the surface inaccessible to the large.

(*2*) Molecules of certain shapes, *i.e.*, chains with several anchoring groups distributed along their length may be adsorbed in lesser quantity than those with the polar groups all at one end, or with a single polar group at one end, for the former lie spread on the surface, occupying an area approaching their lengthwise or curled cross section, while the latter may pack vertically and occupy an area approaching their smallest cross section.

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[156] Patrick and Jones, *J. Phys. Chem.*, 29, 1 (1925).

[157] *Technique of Organic Chemistry*, A. Weissberger, Ed., Vol. II (*Catalytic, Photochemical, and Electrolytic Reactions*), Interscience, New York, 1948.

[158] Broda and Mark, *Z. physik. Chem.*, A180, 392 (1937); Baum and Broda, *Trans. Faraday Soc.*, 34, 797 (1938).

(C) The mutual interactions between adsorbed molecules which may cause them to adhere laterally may influence the quantity adsorbed by allowing the adsorbed film to bridge roughness and fissures in the adsorbent.[159]

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[159] Bikerman, *Trans. Faraday Soc.*, **34**, 800 (1938); *J. Chem. Phys.*, **9**, 880 (1941).

CHAPTER II

Measurement of Adsorption. Treatment of Data

I. INTRODUCTION

If the interface is examined by measuring concentration differences between it and the contiguous phases, then extent of adsorption is measured. If interfacial tension, contact angle, heat of wetting, or molecular orientation is measured, then information about the interfacial region is obtained in terms of other physical magnitudes. Different aspects of the same phenomenon are being examined, and since these are aspects of the same phenomenon it is to be expected that they will be correlated in a very exact manner. Such correlations will be dealt with below. Their utility is that they can throw some light upon the adsorption process, and that sometimes it is more practical to get at the magnitude of an adsorption by measuring some other closely related aspect of the interface, rather than by measuring the adsorption itself.

The results of adsorption measurements may be recorded in two ways. The amount of substance adsorbed may be calculated as the amount present in the interface *in excess* of what its concentration would be if one of the contiguous phases extended with unchanged concentration into this region. Here, the concentration in the interfacial region is compared with that in one of the phases, and the *difference* between the two concentrations is the quantity of interest. This means that there can be "negative adsorption," since the concentration of the substance in the interface can be less than in the bulk phase. The presence of a positive adsorption of a given substance must in many cases imply that negative adsorption of another has also occurred unless the adsorption is accompanied by an increase in density of the material of the interface. At gas–solid interfaces, where the gas may be condensed to some extent, positive adsorption of one component may not imply negative adsorption of another, and this may occur at other interfaces also. The method of evaluating this excess is so to choose the location of the interface (considered to have its origin at a geometrical surface for purposes of the calculation) that the total amount of a chosen "reference component" is the same *as if* both bulk phases remained homogeneous right up to the interfacial surface, and then to determine the excess per unit area of the other components over the amounts that would have been present if both bulk phases had remained homogeneous up to the chosen surface.

When dealing with adsorption at solid–gas or solid–liquid interfaces, another method of recording adsorption is often used. Here the amount of substance adsorbed is considered to be the total amount of the substance adhering to the solid at the interface. This is usually determined by calculation from the change in pressure or concentration of the substance in the other phase following the establishment of equilibrium with the solid. The two methods of recording adsorption are interconvertible. The data obtained in adsorption *experiments* may be recorded in various ways, depending on the way in which the experiment is carried out or the data calculated and plotted. The most common and at the same time practical method of recording adsorption data is in the form of an adsorption isotherm in which the specific amount of the substance adsorbed (whether in moles per gram of adsorbent, or per unit area of interface, or some similar unit) is plotted against the equilibrium concentration of the substance. If the substance is a gas the concentration is recorded in terms of pressure, or partial pressure. If the substance is in solution, grams per liter, moles per liter, mole fraction, etc. may be used. These data are taken at a definite temperature, which gives the curve its name "isotherm." Instead of taking the specific amount of substance adsorbed and the pressure (or concentration) as variables, with temperature constant, one may take the temperature as variable and keep the pressure constant, which yields an adsorption isobar, or one may let pressure and temperature be the variables and keep the specific adsorption constant, and thus obtain an adsorption isostere. Isobar and isostere plots are not very common in organic chemical uses. The three variables can be plotted on a surface. Since the adsorption isotherm is probably the most useful method of recording data, little attention will be given to isobars and isosteres.

II. SOLID–GAS INTERFACE

Measurement of adsorption at this interface has been described for a special purpose in Volume I of this series.[1] A thorough treatment may be found in Brunauer's monograph.[2] As was stated in the preface the subject will not be discussed here, except insofar as necessary to the clarification of the behaviors at other interfaces.

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[1] Harkins, in Weissberger, ed., *Physical Methods in Organic Chemistry*. 2nd ed., Interscience, New York, 1949, Part I, p. 466 ff.

[2] S. Brunauer, *The Adsorption of Gases and Vapors*, Vol. I, *Physical Adsorption*. Princeton Univ. Press, Princeton, 1943.

1. Types of Isotherms

Brunauer, L. S. Deming, W. E. Deming, and Teller[3] have classified adsorption isotherms obtained in the physical adsorption of gases and vapors on solid surfaces into five types, idealized illustrations of which are given in Figure II-1. Isotherms of Type I are known as Langmuir isotherms.

Brunauer[2] interprets the isotherms in the following way. Type I represents adsorption in which the surface of the adsorbent eventually becomes covered with a single layer of molecules (unimolecular or monomolecular adsorption), whereupon no further adsorption occurs, since the surface is covered and no space contiguous to the solid surface is available. Type II isotherms (S-shaped isotherms) are found when the adsorbent attracts the adsorbed molecules more strongly than they attract each other; thus the first part of the curve represents the adsorption which predominates at the lower pressures (concentrations) but which falls off as the surface is covered, giving way to the interactions of the molecules of adsorptive. These form clusters of molecules on the surface and thus lead to thick films (multimolecular or polymolecular adsorption) which increase in thickness as the pressure approaches the vapor pressure.

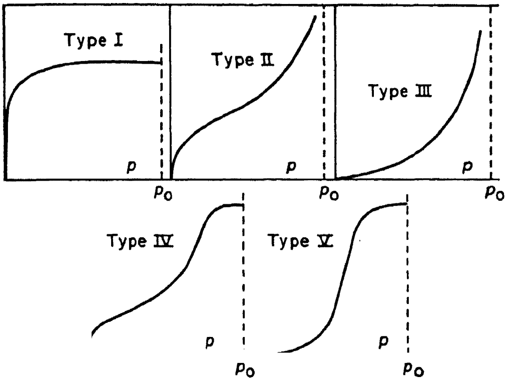

Fig. II-1. Five types of van der Waals adsorption isotherms.[3] $V_{ads.}$ is the volume of gas adsorbed per gram of adsorbent; p is the equilibrium pressure at which the adsorption has occurred; p_0 is the saturation vapor pressure of the adsorptive. These isotherms are found in the adsorption of gases and vapors on solids.

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[3] Brunauer, L. S. Deming, W. E. Deming, and Teller, *J. Am. Chem. Soc.*, **62,** 1723 (1940).

Type III isotherms are found where the attraction between the adsorbent and the adsorbed molecules is small, but enough to supplement the aggregating tendency of the molecules on the surface. Isotherms of Types IV and V are thought to occur where there are pores and capillaries in the solid adsorbent. These become filled with the adsorptive molecules at some pressure below p_0. The first parts of these curves are like those of II and III, and for the same reasons, but the upper parts of the two curves are alike and it is suggested that the shape may be accounted for by the filling of capillaries. This is completed at a pressure below p_0 because the last layer adsorbed in the capillary is attracted from both sides and so condenses more readily.

2. Theories of Adsorption

Langmuir[4] derived an equation which describes the adsorption of molecules upon fixed sites on a surface. The *Langmuir equation* was derived from the consideration that a gas molecule striking an impermeable and perfectly homogeneous solid surface may either rebound immediately or else condense for an appreciable period upon the surface. Langmuir also considered that in the cases under investigation by him the surface forces of attraction were short-range forces, so that absorbed films were only one molecule thick on the average. Under these limitations the rate of condensation of the adsorptive on the surface could be written as $\alpha\theta\mu$. Here μ represents the amount of adsorptive molecules (gram moles) striking unit surface of the adsorbent per second; θ represents the fraction of surface which is bare and so available for condensation of adsorptive, the already covered part of the surface being considered to hold a second layer so feebly that a molecule striking it evaporates at a rate effectively equivalent to a reflection; α is a proportionality constant which is usually close to but never exceeds unity. Molecules evaporate from the surface at a rate $\nu_1\theta_1$, where θ_1 is the fraction of surface actually covered by adsorptive, and ν_1 is the rate of evaporation from a completely covered surface. At equilibrium the rate of condensation (adsorption) is equal to the rate of evaporation (desorption), whence:

$$\alpha\theta\mu = \nu_1\theta_1$$

Since:

$$\theta + \theta_1 = 1$$

then:

$$\theta_1 = \alpha\mu/(\nu_1 + \alpha\mu) \tag{1}$$

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[4] Langmuir, *J. Am. Chem. Soc.*, 38, 2221 (1916); 40, 1361 (1918).

Comparing this equation with an isotherm of Type I (Fig. II-1), it is evident that, as in the isotherm, at low pressures the amount of surface covered (θ_1) will be nearly proportional to the pressure (μ is related to the pressure p thus:

$$\mu = 43.75 \times 10^{-6} p/(MT)^{1/2}$$

where M is the molecular weight of the gas and T the absolute temperature). As the pressure increases θ_1 increases more slowly and finally the surface becomes saturated ($\theta_1 = 1$). The extent of adsorption is then independent of the pressure. In a later paper Langmuir extended his calculations to surfaces with more than one kind of elementary space, and to various other types of surfaces and of behavior of adsorbed molecules, and extended it to films more than one molecule in thickness. The Langmuir equation has been thoroughly discussed by Brunauer,[5] who has also given thermodynamic and some statistical derivations of the theory.

The Langmuir equation may be rewritten in various forms. The constants α and ν_1 may be combined:

$$\beta = \alpha/\nu_1$$

then:

$$\theta_1 = \beta\mu/(1 + \beta\mu) \tag{2}$$

The fraction of surface covered, θ_1, is proportional to the number of moles of adsorptive absorbed divided by the area of the interface, or to the number of grams adsorbed (x) divided by the mass of adsorbent (m), assuming equal masses to have equal surface areas. Then, in the latter case:

$$\theta_1 = kx/m$$

As pointed out above, μ is proportional to the pressure, whence:

$$x/m = k_1 k_2 p/(1 + k_1 p) \tag{3}$$

Taking θ_1 as equal to the ratio of the volume of gas (v) removed by adsorption to the surface at a pressure p to the volume which would be adsorbed (v_m), if the surface were completely saturated with a unimolecular layer,[6] that is:

$$\theta_1 p = v/v_m$$

then:

$$v = v_m bp/(1 + bp) \tag{4a}$$

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[5] S. Brunauer, *The Adsorption of Gases and Vapors,* Vol. I, *Physical Adsorption.* Princeton Univ. Press, Princeton, 1943.

[6] Brunauer, *loc. cit.,* p. 64.

or:
$$p/v = 1/v_m b + p/v_m \tag{4b}$$

If in equation (3) $p/(x/m)$ is plotted against p, or in equation (4) p/v is plotted against p, straight lines should be obtained. Brunauer has emphasized that the constants b and v_m are neither arbitrary nor empirical constants and that for the Langmuir equation to be considered applicable to a given set of data not only must the straight line plot be obtained but also the evaluation of b and v_m from the slope and intercept of the line must yield reasonable values. It may be noted that the area of the absorbent could be obtained from v_m if the cross-sectional area of the adsorbed molecule were known, and the monolayer were tightly packed.

The adsorption equation of Langmuir is limited in scope. The equation was derived to meet a limited objective and when evaluated from this point of view it is seen to have contributed to the clarification of the subject and to the correlation of many data. Clarification has also arisen in those situations in which the Langmuir equation was found to be inapplicable.

A very great advance in the direction of a general theory of physical adsorption was made by Brunauer, Emmett, Teller, L. S. Deming, and W. E. Deming.[7] First they generalized the treatment of Langmuir and were able successfully to account for the three types of isotherms I, II, and III (Fig. II-1); in the later paper a still more general equation was derived which was adequate to describe satisfactorily the shapes of all five isotherms throughout the range of adsorption, as well as to calculate the effects of temperature change upon the adsorptions.

The following fundamental assumptions were made: the area of the total adsorbing surface was measured in terms of the cross-sectional area of the adsorptive molecules, and this was assumed to be the same as that in the liquid substance. The first layer of adsorbed molecules is held to the adsorbent by a force which is related to the average heat of adsorption of the first layer and to the temperature. It is assumed also that the adsorptive forces that bind the first layer of molecules to the adsorbent do not reach much beyond this layer, so that the heat of adsorption of the second, third, and higher layers will be close to the heat of liquefaction (condensation) of the gas.

Detailed discussion and derivation of their equations do not belong here. It is found in the papers referred to, and in Brunauer's book. The Brunauer, Emmett, and Teller (BET) equation is:

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[7] Brunauer, Emmett, and Teller, *J. Am. Chem. Soc.*, 60, 309 (1938); Brunauer, L. S. Deming, W. E. Deming, and Teller, *ibid.*, 62, 1723 (1940).

$$\frac{p/p_0}{v(1 - p/p_0)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c}\left(\frac{p}{p_0}\right) \qquad (5)$$

In this expression p is the equilibrium pressure at which a volume v of gas is adsorbed; p_0 is the vapor pressure of the liquid adsorptive and c is the constant involving the heat of adsorption:

$$c = [(a_1b_2)/(a_2b_1)]e^{(E_1 - E_L)/RT} \qquad (6)$$

The constant $(a_1b_2)/(a_2b_1)$ is the "ratio of evaporation-condensation coefficients for the adsorbed layers," and often has a value near unity.[8] E_1 is the average heat of adsorption of the first adsorbed layer; E_L is the heat of liquefaction of the adsorptive.

A plot of $(p/p_0)/v(1 - p/p_0)$ against p/p_0 gives a straight line over the region in which this equation holds. The intercept of this line is $1/v_m c$ and the slope is $(c - 1)/v_m c$. If the adsorption is carried out at different temperatures $(a_1b_2)/(a_2b_1)$ and $(E_1 - E_L)$ can be determined, providing $(E_1 - E_L)$ is not very dependent on the temperature, by plotting the straight line, log c against $1/T$.[9] The slope of this line serves for the evaluation of $(E_1 - E_L)$ and the intercept for $(a_1b_2)/(a_2b_1)$.

Two other theories may be mentioned: the potential theory and the capillary condensation theory. The former was advanced by Polányi[10] and originally was derived on the assumption that the forces which brought about adsorption to solid surfaces extended quite some distance out from the surface so that several layers, or an "atmosphere" of molecules might be held to the surface. This kind of interaction may operate in certain instances,[11] but in the majority of cases the forces operating seem to be of short range. Polányi's theory was modified to meet this situation, and, according to Brunauer,[12] it is the only theory of physical adsorption that can handle quantitatively adsorption on a strongly heterogeneous surface.

The capillary condensation theory of Zsigmondy[13] involves the idea that many adsorption phenomena can be explained by the condensation of a vapor in a capillary at lower vapor pressures than normal, so that those adsorbents which have fine pores can take up adsorptives by a process of condensation in the capillaries. The condensation occurs at pressures below the normal vapor pressure. It appears that capillary condensation does play a role in many adsorptions.[14]

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[8] But see T. L. Hill, *J. Chem. Phys.*, 16, 181 (1948).

[9] Davis and DeWitt, *J. Am. Chem. Soc.*, 70, 1135 (1948).

[10] Polányi, *Verhandl. deut. physik. Ges.*, 1916, 55; Goldmann and Polányi, *Z. physik. Chem.*, A132, 321 (1928).

[11] Polányi, *Trans. Faraday Soc.*, 28, 316 (1932); see also Henniker and McBain, *Science*, 109, 286 (1949).

[12] S. Brunauer, *The Adsorption of Gases and Vapors*, Vol. I, *Physical Adsorption*. Princeton Univ. Press, Princeton, 1943.

[13] Zsigmondy, *Z. anorg. Chem.*, 71, 356 (1911).

A number of alternative equations and modifications of the BET equation for handling gas adsorption data have been derived on various assumptions.[15]

3. Surface Area of a Solid

The determination of surface area has been described in Volume I of this series.[16] A brief discussion of the implications of the concept is, however, necessary.

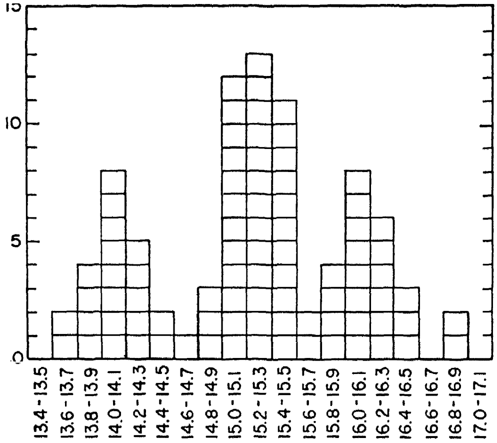

Fig. II-2. Distribution of molecular areas of nitrogen on 86 solids as calculated from the theories of Brunauer, Emmett, and Teller, and Harkins and Jura.[17] (Abscissa is the calculated area of adsorbed N_2 molecule, $A.^2$)

The principle on which area determination is based requires a knowledge of the number of molecules in the unimolecular layer per gram of adsorbent and the average cross-sectional area of the molecule. Investigations of Harkins and his coworkers[17] indicate that the mean area available to the molecule of nitrogen in the first layer of condensed films is not a constant (see Fig. II-2) but varies with the nature of the substrate, a finding which supports other knowledge of the effect of substrates on phase changes in monolayers generally. Though this introduces some uncertainty into the values for areas of some very polar adsorbents, it does not seriously reduce the utility of the BET method for determining areas to nitrogen. A useful compilation of data on areas of adsorbents is given by Deitz[18] (see Chapter VII, and Table VII-1).

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[14] C. Pierce, Wiley, and R. N. Smith, *J. Phys. & Colloid Chem.*, 53, 669 (1949).

[15] Kistler, Fischer, and Freeman, *J. Am. Chem. Soc.*, 65, 1909 (1943); Pickett, *ibid.*, 67, 1958 (1945); Anderson, *ibid.*, 68, 686 (1946); Anderson and Hall, *ibid.*, 70, 1727 (1948).

[16] Harkins, in Weissberger, ed., *Physical Methods of Organic Chemistry.* 2nd ed., Interscience, New York, 1949, Part I, p. 466 ff.

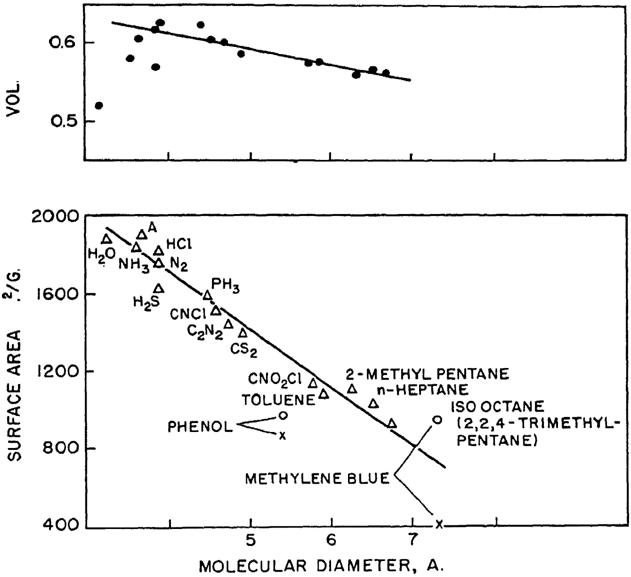

Fig. II-3. The upper curve is a plot of the molecular diameter of the adsorptive against the volume of adsorptive (calculated as a liquid) taken up by the charcoal CWSN 19 at a partial pressure of 0.99. The lower curve is a plot of the surface areas of the charcoal calculated by means of the same adsorptives. The points indicated by open circles are from data by Young for the adsorption of phenol and methylene blue from solution onto crushed (100 mesh) charcoal samples; those marked x are for uncrushed samples of charcoal for these same two adsorptives.[19]

It would appear that the question "What is the surface area of a solid adsorbent?" is meaningless when it implies that an absolute notion of area, derived at the macroscopic level, is transferable to the measurement of the area of surfaces with roughness or porosity of molecular dimensions. For example, the surface area of uniform bubbles, or fire-polished glass beads, or regular crystals which can be measured by means of a traveling microscope or other similarly calibrated instrument does have some meaning in ordinary usage; however, a porous charcoal may have a different "area" for each measuring instrument used: helium; nitrogen; water; x-rays; electron diffraction; etc. This has been graphically presented by Emmett[19] (see Fig. II-3) in a review of the problems met in measurements of adsorption and pore size of charcoals and chemically treated charcoals. *The* area of such a charcoal cannot be specified.

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[17] Harkins and Jura, *J. Am. Chem. Soc.*, **66**, 1366 (1944); Harkins, *Science*, **102**, 263 (1945).

[18] Deitz, *Ann. N. Y. Acad. Sci.*, **49**, 315 (1948).

The root of the problem is that the geometrical concept of a crack or fissure, or of a capillary with a circular or rectangular cross section, cannot reasonably be transferred to molecular dimensions. Geometrical area is calculated in terms of surfaces which may be plane, or curved. Here, any small portion of the surface area is like any other. At the molecular level there are no geometrically plane surfaces, but rather spaces above and between molecules and mosaics of different kinds. The nature, and sometimes the arrangement, of the mosaics differs with distance from the "surface." This does not mean that it is impossible to relate extent of adsorption to the properties of surfaces of adsorbents.

The amount of substance that can be adsorbed at a solid surface, then, depends not only on the physicochemical interactions between the phase and the adsorptive molecules but also on the accessibility of the "surface" of the solid adsorbent to the molecules of the mobile phase. The former factor can be evaluated in terms of changes in potential energy upon adsorption as in the case for mobile interfaces; the latter involves considerations of shape of adsorptive molecules *vis-a-vis* the geometry of the surface. The accessibility may influence the physicochemical interactions in cases where a molecule in a small capillary may be held on more than one side, or where in filling up a larger capillary from the walls inward, the last layer of adsorptive is attracted from more than one direction.[20]

III. VAPOR–LIQUID INTERFACE

At the vapor–solid interface there is usually little doubt about the location of at least one of the boundaries of the interface. If the adsorptive is insoluble in the solid, then adsorption occurs on the surface of the solid. There may be some question in certain cases about the other boundary of the adsorbed layer, but at least the one boundary of the interface is reasonably definite. All nonmobile interfaces have this simplifying feature, and the mobile interfaces between insoluble monolayers and the liquid substrates usually also show this clear boundary to the adsorbed film. However, the situation is not so simple with mobile interfaces containing soluble adsorptives, especially if the adsorptive is also volatile. An important feature in calculating adsorption at such interfaces is the decision of how the interface at which the adsorption is calculated is to be located.

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[19] Emmett, *Chem. Revs.*, 43, 69 (1948).

[20] S. Brunauer, *The Adsorption of Gases and Vapors*, Vol. I, *Physical Adsorption*. Princeton Univ. Press, Princeton, 1943.

1. Vapor–Pure Liquid

The direct measurement of concentration at the interface vapor–pure liquid is difficult. At the surface of a pure liquid in equilibrium with its vapor there must be a transition between the bulk liquid phase and the vapor phase. Evidence, gathered by Adam,[21] indicates that the transition is very abrupt. The optical properties of the surfaces of pure liquids in contact with air indicate that within the interface there is a sharp diminution in the surface density.[22,23] This is to be expected on logical grounds, and, according to Raman and Ramdas,[22] was probably first suggested by van der Waals. However, this is not to say that no orientation of the molecules occurs at the surface of the pure liquid.

2. Solution–Vapor

A. INTRODUCTION

In the case of the solution–gas or solution–vapor interface the measurement of adsorption may be made directly or indirectly. Change in surface tension has long been in use as an indirect measure of adsorption. Many equations have been proposed to relate the two.[24] The classical equation is that of Gibbs, which may be stated for a system at constant temperature and pressure, and for unit area of surface, thus:

$$d\gamma = -\Gamma_1\, d\mu_1 - \Gamma_2\, d\mu_2 - \ldots - \Gamma_i\, d\mu_i \tag{7}$$

Here γ is the surface tension, μ_1 is the chemical potential of the first component, and Γ_1 is the adsorption: the excess of component 1 in some arbitrarily placed "surface of discontinuity" over its concentration in the bulk phase.

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[21] N. K. Adam, *The Physics and Chemistry of Surfaces,* 3rd ed., Oxford Univ. Press, London, 1941, p. 5 *et seq.*

[22] Raman and Ramdas, *Phil. Mag.,* (7), 3, 220 (1927).

[23] McBain, Bacon, and Bruce, *J. Chem. Phys.,* **7**, 818 (1939).

[24] Swan and Urquhart, *J. Phys. Chem.,* 31, 251 (1927).

Guggenheim and Adam[25] have discussed the fact that in evaluating the surface excess of a component (its adsorption) in the surface of a solution by the Gibbs method the value obtained would depend on where the dividing, or reference, surface were placed. Commonly, the reference surface used as an origin in the calculation of adsorption is chosen so that for one component, say the solvent, or component 1, the value of the adsorption of that component shall be zero, *i.e.*, "a portion of the liquid containing unit area of surface contains Γ_i moles of each species more than a portion in the interior *which contains exactly the same quantity of the species 1*".[26] Then by definition $\Gamma_1 = 0$. Guggenheim and Adam defined a number of other conventions for placing the reference surface. The above convention is often referred to as $\Gamma_i^{(1)}$, the adsorption of the *i*th component at the interface where that of component 1 is zero.

A procedure that is more advantageous because it fits better with the physical picture is to treat the interface as a region of finite volume located between the bulk homogeneous phases. Guggenheim, and others,[27] have shown in detail how this may be done to yield fundamental thermodynamic equations analogous to those which describe the properties of bulk phases. For the interface between a two-component liquid and the vapor phase at constant temperature, for example, there is obtained the following relation between the surface tension and the partial vapor pressure of a component (the second component):[28]

$$-d\gamma = RT\left\{\Gamma_2 - \frac{x}{1-x}\Gamma_1\right\} d \log p_2 \qquad \text{(const. temp.)} \qquad (8)$$

Here γ is the surface tension; R the gas constant; T the temperature in °K.; p_2 the partial vapor pressure of component 2; x the mole fraction of component 2 in the liquid; Γ_1 the number of moles of component 1 per unit area of the surface film; and Γ_2 the corresponding quantity for component 2.

In the Gibbs relation different values of adsorption may be obtained depending on the convention used in placing the reference dividing surface in the interface.[25] As Guggenheim pointed out[28] the use of the imaginary geometrical surface of origin "was a skillful mathematical device that avoided any necessity of assigning a thickness to the inhomogeneous layer at the interface." In the treatment above (Eq. 8) there is some degree of arbitrariness in the volume taken per unit area of surface film (or "surface phase"), that is in assigning a thickness to the film, in placing the boundaries of the surface phase where it merges into the contiguous bulk phases. However the advantage is gained that per unit area of film the quantity:

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[25] Guggenheim and Adam, *Proc. Roy. Soc. London,* A139, 218 (1933).

[26] Guggenheim and Adam, *ibid.,* A139, 223 (1933).

[27] See Guggenheim, *Trans. Faraday Soc.,* 36, 397 (1940); also earlier work is cited.

[28] Guggenheim, *Research,* Special Supplement No. 2, 11 (1949).

$$\left\{\Gamma_2 - \frac{x}{1-x}\Gamma_1\right\}$$

is invariant with respect to thickness, provided that the inhomogeneous boundary region is included. This quantity is a measure of the adsorption of component 2 relative to component 1, and is equal to $\Gamma_2^{(1)}$ defined above.[26,28] There is a certain indefiniteness about the quantity of liquid in the interior of the bulk phase with which one compares the portion of liquid containing unit area of surface.

Defay[29] has sought to avoid the practical difficulties in applying the Gibbs concept which arise from the use of a geometrical surface. The difficulty of knowing with precision the physical position of the reference surface was evaded by the use of a "reduced adsorbed mass" $\mathbf{m}^a$:

$$\mathbf{m}^a{}_i = m_i - Vc'_i - (m - V\rho')\frac{c'_i - c''_i}{\rho' - \rho''} \tag{9}$$

where the total adsorbed mass of component i ($\mathbf{m}^a{}_i$) is measured in terms of the total volume of the system (V) the specific masses of phases 1 and 2 (ρ' and ρ''); the concentrations of the ith component in phases 1 and 2 (c'_i and c''_i); and the total masses of i and of the system (m_i and m) which are known from the original setting up of the system. The definition says nothing about plane surfaces, surfaces of reference, or necessity for equilibrium. The reduced adsorbed mass is extensive; to convert it to an intensive property of the system it is stated per unit of surface area, thus defining the *reduced adsorption*:

$$\underline{\Gamma}_i = \mathbf{m}^a{}_i/\omega$$

Here ω is the area of the surface in which surface tension is experimentally measured, wherein the real physical system is approached. Defay points out that since the reduced adsorbed mass is independent of the position chosen for the surface, any small error in estimating the area is reflected in the reduced adsorption by only a small error. His papers should be consulted for a complete exposition of the subject.

B. MEASUREMENT OF ABSOLUTE AMOUNT OF ADSORPTION

Many experimental tests of Gibbs' relation have been attempted. Only what appears to be the most elegant test will be described here.

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[29] Defay, *Mém. acad. roy. Belg., Classe sci.*, 20, No. 6 (1946).

Other less satisfactory ones may be found collected in a paper by McBain and DuBois[30] and in more general works.[31] An experimental test of the absolute amount of adsorption was made by McBain and Humphreys[32] by a "microtome method." In this method a microtome blade mounted on a carriage was propelled at a speed of some 35 feet per second along the surface of a solution in equilibrium with its vapor in such a way that the blade "sliced" or scooped from the surface a superficial layer of uniform thickness over a known area. The liquid so removed was collected in a receptacle and after removal was weighed and its concentration compared interferometrically with that of the bulk solution from which the layer was scooped. The observed adsorption $\Gamma_2^{(1)}$ could then be calculated from the concentrations of the two samples, the weight of solution collected by the blade, and the area of surface which was shaved. The predicted adsorption could be calculated from measurements of surface tension and concentration by means of the Gibbs relation. This equation was thus tested by the measurement of the concentration of a solute *in the interface*. Using this method the observed and predicted adsorptions of *p*-toluidine, phenol, and caproic and hydrocinnamic acids at the surfaces of water solutions of various concentrations were compared. The same experimental method was used later by McBain and Swain[33] with solutions showing positive and negative adsorptions. The results are in Table II-1. Agreement between observed adsorptions of these substances and those predicted by the Gibbs relation was considered satisfactory.

The adsorption at the solution–gas interface has, at least in certain cases, then been correlated with change in surface tension through direct measurement. Since surface tension changes are easier to measure than concentrations at the interface it is common to rely upon the former measurement as indicative of extent of adsorption. The argument holds for all mobile interfaces. A distinction has to be made in some cases between systems containing soluble and those containing insoluble adsorptives, for not all methods of measurement are applicable to both.

C. SOLUBLE ADSORPTIVE

The interfacial tension for liquid–vapor or liquid–liquid interfaces may be measured in a variety of ways: by capillary height, drop weight, hanging drop, sessile bubble, bubble pressure, ring, vertical plate, and various other techniques. These have been described in detail by Harkins in

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[30] McBain and DuBois, *J. Am. Chem. Soc.*, 51, 3534 (1929).

[31] J. Rice, in *A Commentary on the Scientific Writings of J. Willard Gibbs*, Vol. I, Donnan and Haas, eds., Yale Univ. Press, New Haven, 1936, p. 557 *et seq.* See also Adam, footnote 21.

[32] McBain and Humphreys, *J. Phys. Chem.*, 36, 300 (1932).

[33] McBain and Swain, *Proc. Roy Soc. London,* **A154**, 608 (1936).

TABLE II-1
Direct Measurement of Adsorption[a]

Substance	No. of experiments	Conc., g. subst. per. 1000 g. water	$\Gamma_2^{(1)}$, g./cm.^{2} × 10^8	
			Average observed	Predicted from Gibbs eq.
Hydrocinnamic acid......	25	3.987	7.5	7.5
	25	3.002	6.8	7.3
	7	1.501	5.0	5.2
	10	1.498	5.3	5.2
Phenol..................	5	30.0	5.5	4.9[b]
	10	20.0203	5.3	4.8[b]
	10	5.0179	2.3	2.1[c]
Sodium chloride[d].........	25	135.0276	−0.43	−0.37
	25	99.0213	−0.25	−0.29
	9	46.0171	0.0	−0.17

[a] Values obtained by McBain and Swain[33] by the microtome method—summary of their Tables I, II, III, and IV.

[b] Progressive dilution of the solution occurred.

[c] Concentration of the solution remained constant.

[d] The measurements with sodium chloride were made under unfavorable conditions due to the high concentrations of the solutions, the small differences involved, and mechanical difficulties concerned with evaporation.

Volume I of this series,[34,35] and will not be treated here. Harkins has also given criteria for the choice of method in a particular application.[34]

In the presence of very surface active agents the measurement of surface tension may become quite difficult. Bartell[36] points out that the capillary rise method may give unreliable results due to extreme difficulties in obtaining equilibrium. In these cases also the bubble-pressure method is impractical, also giving high results. The ring method is very useful but is not recommended for precision measurements.[37] The best methods with these solutions, according to Bartell, are the pendant drop and sessile-bubble methods. These comments, he says, apply also to liquid–liquid interfaces.[36]

Types of Data. McBain and coworkers[38–41] have recognized three classes, or types, of surface tension–concentration curves for solutions. In Type 1 the surface tension falls rapidly at first, then more slowly with increasing concentration. This type of curve shows that positive adsorption of solute is occurring. Type 2 curves show a rise in surface tension with concentration. Here the solvent, rather than the solute, is in excess in the surface. In Type 3 curves there is an initial extremely steep fall in surface tension in very dilute solutions. The surface tension then passes through a minimum, and, with further increase in concentration, rises somewhat to a plateau considerably lower than the value for the pure solvent.

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[34] Harkins, in Weissberger, ed., *Physical Methods of Organic Chemistry,* 2nd ed., Interscience, New York, 1949, Part I, p. 355 ff.

[35] H. Freundlich, *Colloid and Capillary Chemistry,* Trans. from 3rd ed., Methuen, London, 1926; E. K. Rideal, *An Introduction to Surface Chemistry,* 2nd ed., Cambridge Univ. Press, London, 1930, see especially Chapter 9; N. K. Adam, *The Physics and Chemistry of Surfaces,* 3rd ed., Oxford Univ. Press, London, 1941; A. M. Schwartz and J. W. Perry, *Surface Active Agents,* Interscience, New York, 1949.

[36] Bartell, *Ind. Eng. Chem.,* 33, 737 (1941).

[37] Hauser, Edgerton, Holt, and Cox, *J. Phys. Chem.,* 40, 973 (1936).

[38] McBain and Perry, *Ind. Eng. Chem.,* 31, 35 (1939).

[39] McBain and Spencer, *J. Am. Chem. Soc.,* 62, 239 (1940).

[40] McBain and Sharp, *ibid.,* 63, 1422 (1941).

[41] McBain, Ford, and Wilson, *Kolloid-Z.,* 78, 1 (1937).

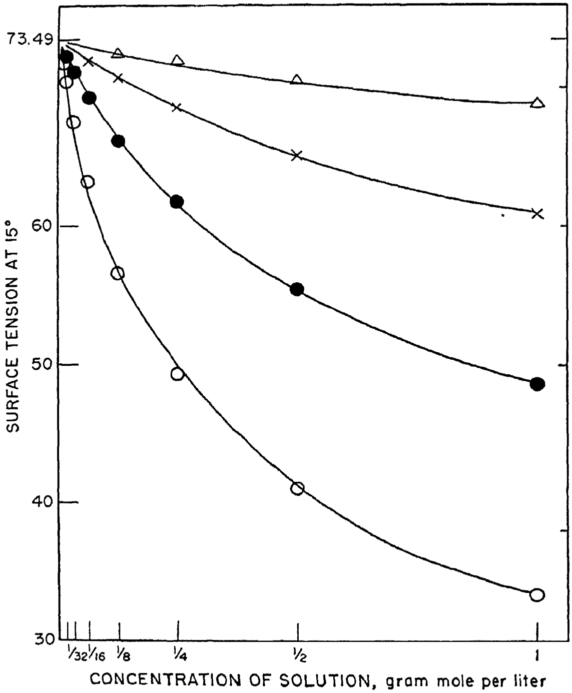

Fig. II-4. Plot of Traube's data for the surface tensions of solutions of fatty acids. The concentration of the solution of fatty acid, in gram moles per liter, is plotted against the surface tension of the solution in dynes per centimeter, at 15°. The surface tension of pure water at 15° is 73.49 dynes per centimeter. (△) formic acid; (×) acetic acid; (●) propionic acid; (○) butyric acid.

Curves of Type 1 indicate positive adsorption over the concentration range. Such curves are shown in Figure II-4. The study of curves of this sort for homologous series of lower aliphatic acids, esters, and other substances led Traube[42] to enunciate the rules that (*1*) at sufficiently low concentrations surface tension–concentration curves are linear and (*2*) there is a regular increase in the slope of the initial, straight-line part of the curves for each additional CH_2 in the molecule when lower aliphatic homologs are compared.

Considerable information may be obtained from surface tension–concentration isotherms. Traube's first rule states that at sufficiently low concentrations:

$$\gamma_0 - \gamma = \alpha c \tag{10}$$

where γ_0 is the surface tension of pure solvent; γ that of the solution of concentration c; and α is Traube's constant, the initial slope of the curve:

$$\alpha = -(d\gamma/dc)_{c\rightarrow 0} \tag{11}$$

Szyszkowski[43] fitted an empirical equation to these isotherms which Langmuir[44] combined with the Gibbs adsorption equation to give an equation for adsorption at the liquid–vapor interface. This equation has the same form as his equation for adsorption at the gas–solid interface (Eq. 3):

$$\Gamma = K\alpha c/(1 + \alpha c)$$

At low enough concentrations this reduces to a linear relation:

$$\Gamma = K\alpha c$$

in which Γ is the adsorption of solute (gram moles per square centimeter of surface), c is the equilibrium bulk concentration (gram moles per cubic centimeter), K is a constant for all members of a given homologous series, and α is the Traube constant. Langmuir also showed how Traube's second rule might be derived. A thermodynamic derivation of this rule has been given by Ward and Tordai.[45]

Langmuir[44] and others[45,46] have obtained from these curves expressions by means of which the free energy of transference of solute molecules from bulk solution to interface could be calculated. Ward and Tordai[45,47] have calculated the free energies of adsorption, the activities, and activity coefficients of several solutes in the solution–vapor interface. Some of their data are presented in Table II-2. The molecular interpretations of some of this work are given in Chapter I.

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[42] Traube, *Ann.*, **265**, 27 (1891).

[43] Szyszkowski, *Z. physik. Chem.*, **64**, 385 (1908).

[44] Langmuir, *J. Am. Chem. Soc.*, **39**, 1848 (1917), see p. 1883.

[45] Ward and Tordai, *Trans. Faraday Soc.*, **42**, 413 (1946).

[46] Merckel, *Kolloid-Beihefte*, **45**, 413 (1937).

[47] Ward and Tordai, *Trans. Faraday Soc.*, **42**, 408 (1946).

TABLE II-2

Free Energies of Adsorption of Some Fatty Acids and Phenol at the Aqueous Solution–Air Interface

Solute	Thickness of monolayer, A.	Standard free energy of transference of solute from bulk to surface	
		k.cal./mole	erg/molecule
C_3H_7COOH..........	9.86	2.45	16.9×10^{-14}
C_4H_9COOH..........	10.61	3.18	21.9
$C_5H_{11}COOH$..........	11.25	3.72	25.6
$C_6H_{13}COOH$..........	11.64	4.52	31.1
$C_7H_{15}COOH$..........	11.84	5.40	37.2
$C_8H_{17}COOH$..........	11.96	6.10	42.0
$C_9H_{19}COOH$..........	12.18	7.06	48.6
C_6H_5OH.............	5.75	2.28	15.7

Curves of Type 2 in McBain's classification are found in certain cases of extremely soluble substances; *e.g.*, salts, and sucrose, in water. There is still some question about the shape of these curves. It has been thought that such substances as sodium chloride, etc., raise the surface tension of water at all concentrations of their solutions. But Jones and Ray,[48] using a very sensitive differential capillarimeter, with which they were able to claim results with an error of not more than 0.002% in the average, felt that they could show that at very low concentrations perhaps below 0.002 *N*, the surface tension of water was lowered by inorganic salts, the surface tension–concentration curve showing a minimum. Some question has arisen whether this minimum actually exists, or is due to the method of measurement or interpretation.[49] Jones and Ray[50] felt that the probabilities are that it exists.

McBain and others have observed minima in some surface tension–concentration curves (*Type 3*, Fig. II-5). The subject is reviewed by McBain.[51] The curves pass through a minimum in very dilute solution and then rise to a somewhat higher value, where they level off and perhaps slowly decline. The width and depth of the minimum region vary with the adsorptive.

Considerable effort has gone into the investigation of the causes for this behavior. It would appear that the low value represented by the sharp drop to the minimum value (Fig. II-5) is due to the presence (often in extremely small amount) of impurity in the adsorptive. It is known[52] that the addition of electrolyte to solutions of paraffin-chain salts can exert a strong effect on the surface activity of these detergents, the adsorbed molecules of which are certainly ionized. However, the amount of added electrolyte must be quite large—some twenty times the amount of the detergent.[53,54] In most cases, however, the impurity is a strongly adsorbed

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[48] Jones and Ray, *J. Am. Chem. Soc.*, 59, 187 (1937).

[49] Dole and Swartout, *J. Am. Chem., Soc.*, 62, 3039 (1940); McBain and Sharp, *ibid.*, 63, 1422 (1941); Dole, *ibid.*, 60, 904 (1938); Long and Nutting, *ibid.*, 64, 2476 (1942); Coolidge, *ibid.*, 71, 2153 (1949); Bikerman, *Trans. Faraday Soc.*, 34, 1268 (1938); Langmuir, *Science*, 88, 430 (1938); *J. Chem. Phys.*, 6, 873, 894 (1938); Jones and Frizzell, *J. Chem. Phys.*, 8, 986 (1940).

[50] Jones and Ray, *J. Am. Chem. Soc.*, 63, 288 (1941).

[51] McBain, in J. Alexander, *Colloid Chemistry*. Vol. V, Reinhold, New York, 1944, p. 102.

[51a] McBain, Vinograd, and Wilson, *J. Am. Chem. Soc.*, 62, 247 (1940).

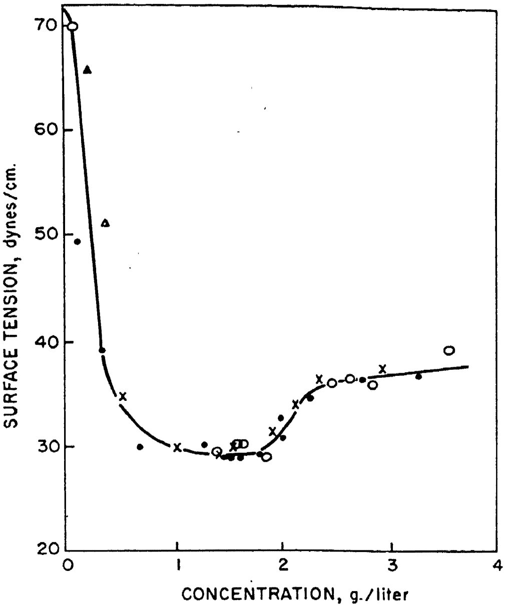

Fig. II-5. Surface tension curve with a minimum.[51a] Surface tension of lauryl sulfonic acid, showing a curve of *Type 3*. The values were obtained by the following methods, at the times stated, and represent final lowering of the surface tension: (○) PLAWM trough at 60 min.; (△) PLAWM trough at 10 hrs.; (×) Wilhelmi method at 45 min. at least; (●) ring method at 1 to 2 days; (▲) capillary rise method, time not stated.

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[52] Powney and Addison, *Trans. Faraday Soc.*, 33, 1243, 1253 (1937); Cassie and Palmer, *ibid.*, 37, 156 (1941).

[53] G. D. Miles and L. Shedlovsky, *J. Phys. Chem.*, 48, 57 (1944).

[54] G. D. Miles, *J. Phys. Chem.*, 49, 71 (1945).

organic substance, ionic or nonionic in nature, which is present in the adsorptive. Thus Miles and Shedlovsky[53] showed that the addition of traces of dodecanol to sodium dodecyl sulfate produced a minimum in the surface tension–concentration curve. Dodecanol is an intermediate in the preparation of sodium dodecyl sulfate and is not very soluble in water. These authors also produced minima in the curves by introducing a different kind of impurity. To the sodium dodecyl sulfate was added sodium hexadecyl sulfate to the extent of 1% of the other adsorptive. The minimum here was produced by a soluble but very surface-active impurity. This work was extended by Miles[54] to liquid–liquid interfaces, and has been further generalized by Shedlovsky, Ross, and Jakob.[55]

The rapid fall in surface tension with concentration in the presence of an impurity which is very surface active explains the first parts of the curves which show minima. The questions that next arise are why there is a minimum, with subsequent *increase* in surface tension, and why the curve then levels off with increasing concentration (Fig. II-5).

The existence of the minimum in the curve, together with the evidence for strong adsorption even though the surface tension–concentration curve shows a slope of zero at the minimum, led some investigators to question the applicability of the Gibbs adsorption equation to these systems. The evidence that impurities are present, together with evidence gathered from other properties of these solutions,[56] seems to have resolved this question. The minima appear to occur in the region of the critical concentrations for micelle formation of these adsorptives. At this point micelles begin to appear in quantity, and they solubilize the impurity that caused the excessive lowering of the surface tension, thus changing its chemical potential and causing the surface tension–concentration curve to rise up to the point of equilibrium between adsorptive molecules and micelles.

The horizontal parts of the surface tension–concentration curves are thought, then, to represent the region in which the molecules of adsorptive are in equilibrium with micelles. Thus the bulk concentration of single molecules is approximately independent, over this region, of the stoichiometric concentration. Added adsorptive is taken up in micelle formation. This latter sets in over a relatively limited range of concentration.[57] The problem is seen to lie not with the Gibbs equation for adsorption but with the correct application of it which requires a knowledge of the composition of the system involved.

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[55] L. Shedlovsky, Ross, and Jakob, *J. Colloid Sci.*, 4, 25 (1949).

[56] Reviews by McBain, in J. Alexander, *Colloid Chemistry*, Vol. V, Reinhold, New York, 1944, p. 102; also ref. 55, above.

[57] A. E. Alexander, in E. K. Rideal, *Colloid Science*. Chemical Pub. Co., Brooklyn, 1947.

D. INSOLUBLE ADSORPTIVE

When the liquid–vapor or liquid–liquid interface contains a nearly insoluble substance the methods of measurement of adsorption become limited, but in some respects easier. Since the substance adsorbed is insoluble in the adjacent phases, it follows that "all" the molecules are present in the interface, and an extreme case of adsorption is being dealt with: the concentrations in the bulk phases are neglected and the adsorption is determined by dividing the number of molecules of adsorptive present by the area of the interface. Borderline cases occur, of course, when the adsorptive is slightly soluble. These will not be discussed to any extent since their behavior appears to follow the intermediate course between the behaviors of soluble and insoluble adsorptives. The films of insoluble substances exhibit behaviors which set them apart sufficiently that they have become a special field of study. The behaviors of these films have been extensively treated by Adam[58] and, in a previous volume of this series, by Harkins,[59] and will not be discussed here.

E. VISCOUS INTERFACES

Antonoff[59a] measured the "surface tension" of pastes by means of an apparatus which pulls apart two rods coated with the paste. The surface tension of solids is estimated by the use of pastes. The rationale on which this measurement is based is the Antonoff rule,[59b] that $\gamma_{1,2} = \gamma_1 - \gamma_2$; where γ_1 is the surface tension of one medium (the solid); γ_2 that of the other medium; and $\gamma_{1,2}$ that of the interface. γ_2 can be chosen so that $\gamma_1 - \gamma_2 = \gamma_{1,2} = 0$; the criterion for $\gamma_{1,2}$ being that if $\gamma_1 > \gamma_2$ the fluid adheres to the solid, if $\gamma_1 < \gamma_2$ the fluid does not adhere to the solid. If the solid is transparent the paste is forced by suction through a tube of the solid or a plate with a capillary hole. Pastes with lower "surface tension" than the solid will leave a film; those with higher "surface tension" will not wet the walls of the hole and will leave no trace behind. For nontransparent solids a rod of solid with a polished end is inserted through a somewhat larger hole in a plate (say of glass) resting on the paste. The rod is drawn off slowly from the paste. If its "surface tension" is higher than that of the paste it will ascend coated with paste. Tackiness has been discussed by Bikerman.[59c]

[58] N. K. Adam, *The Physics and Chemistry of Surfaces,* 3rd ed., Oxford Univ. Press, London, 1941. See also A. E. Alexander and P. Johnson, *Colloid Science,* Oxford Univ. Press, London, 1949.

[59] Harkins, in Weissberger, ed., *Physical Methods of Organic Chemistry,* 2nd ed., Interscience, New York, 1949, Part I, p. 427 ff.

[59a] Antonoff, *Rubber Age,* November, 1946.

[59b] Antonoff, *J. chim. phys.,* 5, 372 (1907).

[59c] Bikerman, *Trans N. Y. Acad. Sci.,* 1947, 273; J. J. Bikerman, *Surface Chemistry for Industrial Research,* Academic Press, New York, 1947.

IV. SOLID–LIQUID INTERFACE

1. Solid–Pure Liquid

When the system to be examined consists of a pure liquid and a solid the measurement of adsorption is usually made indirectly by observing in the system or in one of the phases a change upon formation of the interface. The heat of wetting is one of the more useful quantities which measure the extent of interaction between a pure liquid and a solid.[60] A quantity of somewhat more restricted applicability is the contact angle, and another, the adhesion tension. A more direct measurement can be made by optical examination of the interface. Wheeler[61] observed that the transition region at the surfaces of metal mirrors immersed in transparent liquids was sharp.

2. Solution–Solid

Measurement of adsorption from *solution* onto a solid surface is usually carried out by observing the difference between the concentration of the solution before the adsorbent is introduced into it and after equilibrium is established. This kind of indirect measurement involves two assumptions: (*1*) that the components of the liquid phase do not dissolve in the adsorbent; and (*2*) that the solvent is not adsorbed to an extent which vitiates the measurement.

In a typical experiment a given weight or volume of solution of known concentration is placed in a glass-stoppered flat-bottom flask. Into this is weighed the required amount of adsorbent, previously dried or otherwise prepared, and the mixture is swirled and placed in a thermostat. The mixture is allowed to stand, with intermittent swirling, until equilibrium is reached. The fluid is removed from the adsorbent and aliquots analyzed for solute. The results are usually visualized by plotting the number of moles apparently adsorbed (disappeared from solution) per unit weight of adsorbent against the equilibrium concentration of the solution, thus yielding an adsorption isotherm. Another, often convenient, way of obtaining these data, is by the use of a countercurrent technique described in Chapter IX.

In measuring adsorption from solution by measuring change in concentration of the solution on addition of the adsorbent, the solution may be removed from the adsorbent by filtration, centrifugation, or decantation.

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[60] Harkins, *loc. cit.*, p. 466 ff.

[61] Wheeler, *Phil. Mag.*, (6), 22, 229 (1911).

If small amounts of liquid and solid are involved, Skau[62] or English[63] tubes may be used to advantage. The concentration of the solution may be measured in any of the known ways, or the adsorbent may be allowed to settle and the concentration of the solution examined *in situ* by optical or other means (ChapterVII).

The adsorption process is usually quite rapid, often being 95 to 99% complete during five minutes at room temperature. However, in careful work, a rate study is always made. A series of identical solutions are treated with equal weights of adsorbent and examined after different intervals. From the resulting data a time of reaction sufficiently long to ensure equilibrium is chosen for the remaining experiments with the solution.

It was pointed out above that in simple measurements of the change in concentration on equilibration of a solution with an adsorbent two assumptions are made: (*1*) that neither the solute nor the solvent dissolves in the adsorbent; and (*2*) that solvent is not adsorbed to an extent which vitiates the results. The first assumption usually holds fairly well, certainly in the case of adsorption on quartz powder, glass spheres, etc., the more dense charcoals, graphite, etc., metals, silica gel, alumina, anatase, and other dense crystalline materials. However, it does not hold for adsorption on zeolitic materials, whether on inorganic zeolites such as Permutit, greensands, etc., or on organic exchange substances such as sulfonated coals, and exchange resins, when the adsorption may occur through an exchange process and solvent can pass into the structure of the adsorbent. It may be stated as a general principle that, whenever an adsorbent swells or shrinks, then absorptive interaction with the liquid phase must be suspected. When the kind of interaction is not clear the noncommittal term "sorption" (due to McBain[64]) is very convenient to use. Even charcoal changes volume slightly during adsorptions.[65]

The second assumption, that solvent is not adsorbed to an extent to vitiate the experimental results, requires some discussion. In a great many of the adsorption experiments reported in the literature the adsorption has been measured from such dilute solution that adsorption of solvent usually can be neglected. In experiments comparing adsorption of different substances from a given solvent the adsorption of solvent probably can be assumed to be a nearly constant factor. In these cases, neglect of the adsorption of the solvent can be justified.

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[62] Skau, *J. Phys. Chem.*, 33, 951 (1929); Skau and Rowe, *Ind. Eng. Chem., Anal. Ed.*, 3, 147 (1931).

[63] English, *Ind. Eng. Chem., Anal. Ed.*, 16, 478 (1944).

[64] McBain, *Z. physik. Chem.*, 68, 471 (1909).

[65] Bangham and Fakhoury, *Proc. Roy. Soc. London,* A130, 81 (1930); Bangham and Razouk, *ibid.*, A166, 572 (1938). For further references, see these two papers, and Wiig and Juhola, *J. Am. Chem. Soc.*, 71, 561 (1949).

Many equations are available to describe the data when adsorption is studied over a narrow range of concentration.[66] The Langmuir equation and the Freundlich equation are often employed. The curves obtained from adsorption data show certain common features. At sufficiently low concentrations the specific amount adsorbed, x/m, is often proportional to the concentration, c, that is:

$$x/m = kc$$

At high concentrations the amount adsorbed sometimes approaches a limiting value, suggesting that the surface of the adsorbent can become saturated with adsorptive. Both of these features have been seen in isotherms for other interfaces.

The equation named after Freundlich may be written:[67]

$$x/m = Kc^n \tag{12a}$$

where K and n are constants. (Sometimes the equation is written:

$$x/m = Kc^{1/n} \tag{12b}$$

where this n would have the value the reciprocal of that in equation 12a.) x is the weight (or number of moles, etc.) of substance adsorbed by m grams of adsorbent. This equation often fits the data of an adsorption from solution over a reasonable range, but it does not reduce to a linear equation at very low concentration, nor does it approach a constant value for the adsorption at higher concentrations. The data fit this equation over the range where a plot of $\log (x/m)$ against $\log c$ is a straight line:

$$\log (x/m) = \log k + n(\log c) \tag{13}$$

The intercept is $\log k$ and the slope is n. Many attempts have been made to give k and n physical meanings, but with uncertain success.[68]

The Langmuir equation:

$$x/m = k_1k_2c/(1 + k_1c) \tag{14}$$

has already been derived (Eq. 3). This equation also often fits the data of an adsorption over a reasonable range. For a given set of data this equation may fit better or over a longer range than the other, while for another set of data the reverse may hold. This equation fits the conditions described above. At low concentrations the equation reduces to:

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[66] H. Freundlich, *Colloid and Capillary Chemistry*, Methuen, London, 1926; N. K. Adam, *The Physics and Chemistry of Surfaces*, 3rd ed., Oxford Univ. Press, London, 1941; Swan and Urquhart, *J. Phys. Chem.*, 31, 251 (1927).

[67] H. Freundlich, *Colloid and Capillary Chemistry*. Methuen, London, 1926.

[68] Linner and Gortner, *J. Phys. Chem.*, 39, 35 (1935).

[68a] H. G. Cassidy and S. E. Wood, *J. Am. Chem. Soc.*, 63, 2628 (1941).

$$x/m = k_1k_2c$$

at high concentrations it approaches:

$$x/m = k_2$$

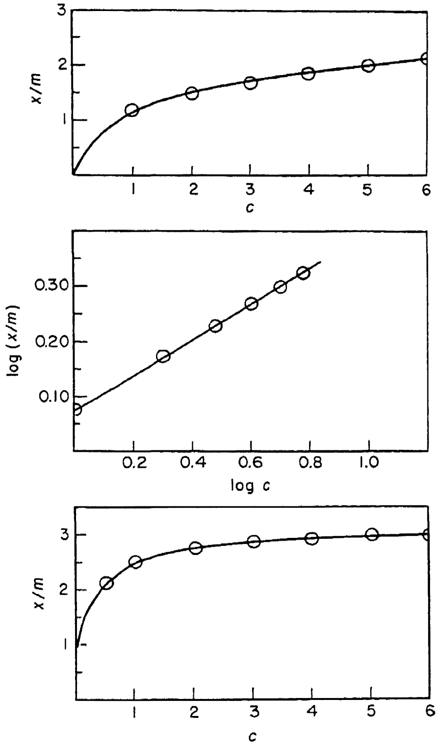

Fig. II-6. Plots of Freundlich and Langmuir isotherms to show the characteristic shapes. *Upper curve:* Freundlich isotherm. The relation plotted is $x/m = kc^n$, where $k = 1.2$ and $n = 0.32$. (This relation fits closely part of the adsorption curve of lauric acid from petroleum ether onto Darco G-60 charcoal.[84a] *Middle curve:* log plot of the data fitted by the Freundlich isotherm. From the plot $\log x/m = \log k + n \log c$ the two constants may be determined. *Lower curve:* Langmuir isotherm. The equation used for plotting is $x/m = k_1k_2c/(1 + k_1c)$, where $k_1 = 4.03$ and $k_2 = 3.13$.

Furthermore, from the derivation k_2 is the amount of adsorptive which would saturate unit surface with a monolayer, and k_1 is the "capillarity" of the substance. If $c/(x/m)$ is plotted against c a straight line should be obtained over the region in which the Langmuir equation holds. This line will have a slope of $1/k_2$ and an intercept of $1/k_1k_2$. If the Langmuir equation were to fit the data for more adsorptions from solution than it does, and if it fit over a greater range, the interpretation of data would be simplified. Plots of Freundlich and Langmuir isotherms are shown in Figure II-6.

Instead of measuring adsorption with a given weight of adsorbent and solutions of different concentration, the measurement may be made with equal quantities of solution of known concentration into which different amounts of adsorbent are weighed. The results of this kind of measurement have sometimes been difficult to interpret, and a considerable literature has grown around them. The curves of adsorption *vs.* amount take different shapes for solutions of different concentration. The factors that influence these results seem to be dispersion of the adsorbent and adsorption of both solute and solvent. Probably other factors also operate.[69] Burgers[70] found the ratio x/m to be a uniform function of the equi-

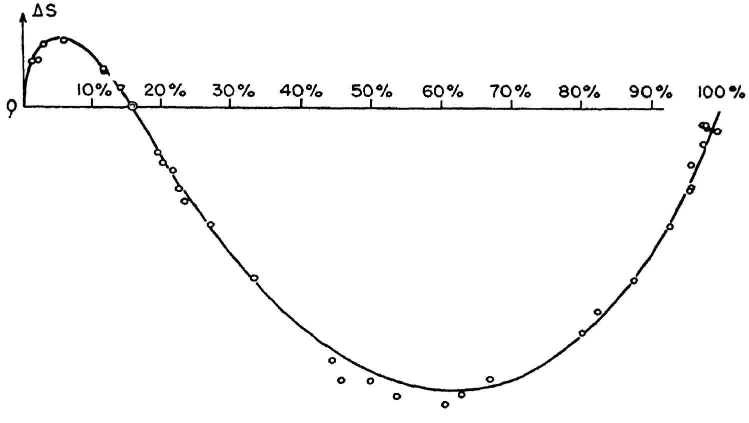

Fig. II-7. Example of an S-shaped isotherm.[70a] The adsorption of acetic acid onto charcoal in the system acetic acid–1,2-dibromoethane is shown. ΔS is the "specific concentration difference," the fall in concentration of acetic acid in the solution produced by 1 g. charcoal in 100 g. solution. On the abscissa is plotted weight percent of acetic acid in the equilibrium solution.

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[69] Wo. Ostwald, *Kolloid-Z.*, 43, 268 (1927); Mehl, *ibid.*, 56, 299 (1930); Roychoudhury, *ibid.*, 57, 308 (1931).

[70] Burgers, *Rec. trav. chim.*, 63, 46 (1944); but see Van Duuren, *ibid.*, 64, 303 (1945).

librium concentration in the adsorption of acetic acid from solutions 0.01 to 0.4 *N* onto deashed Norit, and concluded that decreased specific adsorption with increase in the amount of adsorbent added to a solution was probably solely attributable to exhaustion of the solution.

The adsorption of solvent must be taken into account for very accurate work at low concentrations and for work at high concentrations, as in the study of adsorption from a binary mixture over the range mole fraction 0 to 1. The isotherm curves obtained in such experiments are S-shaped, or of a modified S-shape (see below). An experimental curve is shown in Figure II-7.

Williams[71] attempted to take account of the adsorption of the solvent, and devised a method of determining how much solvent is adsorbed on a solid adsorbent in the case where the same equilibrium is reached in the vapor as in the liquid phase. As a first step the adsorbent is exposed to the vapors of the solution of known initial concentration in an evacuated desiccator until constant weight is reached. It may require a period of 100 days to reach equilibrium. The solution is then analyzed. The adsorbate is now mixed into the solution, and after equilibration the solution is again analyzed. If introduction of the adsorbate produced no change in the concentration of the solution, then equilibrium in the first step is indicated. The concentration on the adsorbent can be determined from the change in concentration of the solution in the first step and the weight of substance (both components) adsorbed in this step. The adsorption of air is ignored.

Other methods of determining the amount of solvent adsorbed have also been devised. De Brouckère[72] removed the adsorbent from the equilibrium solution and, assuming that the adsorbed layer (inorganic substances adsorbed on barium sulfate) adhered to the adsorbent to the point of resisting washing which should remove entrained solution, washed off the excess solution. She also used another method in which, by calculating the adsorption of both components, the change in the volume of the solution could be eliminated. Dobine[73] adsorbed acetic acid from water over the entire concentration range on moist and dried charcoal and from the curves for the two, with certain assumptions, calculated the adsorption of solvent and solute.

[70a] Wo. Ostwald and Schulze, *Kolloid-Z.*, 36, 295 (1925).

[71] Williams, *Medd. Vetenskapsakad. Nobelinst.*, 2, No. 27 (1913).

[72] Pinkus and de Brouckère, *Bull. acad. roy. Belg., Classe sci.*, (5), 13, 415 (1927); *J. chim. phys.*, 25, 605 (1928); de Brouckère, *Bull. soc. chim. Belg.*, 44, 625 (1935); 45, 279, 353 (1936).

[73] Dobine, *Compt. rend.*, 206, 430 (1938); *ibid.*, 212, 155 (1941).

Jones and Outridge[74] determined the volume of liquid taken up by the adsorbent in two ways: one from equilibration with the vapor of the liquid,[75] one from immersion in the liquid. The former is the Williams method.[76] For determining the amount of liquid adsorbed, Jones and Outridge used Bachmann's immersion method.[77] The adsorbent (silica gel) was immersed in the solution and allowed to come to equilibrium. Then it was removed from the solution, quickly dried with filter paper, and weighed. The weight of liquid divided by its ordinary density at the temperature of the experiment gave the volume of liquid adsorbed.[78]

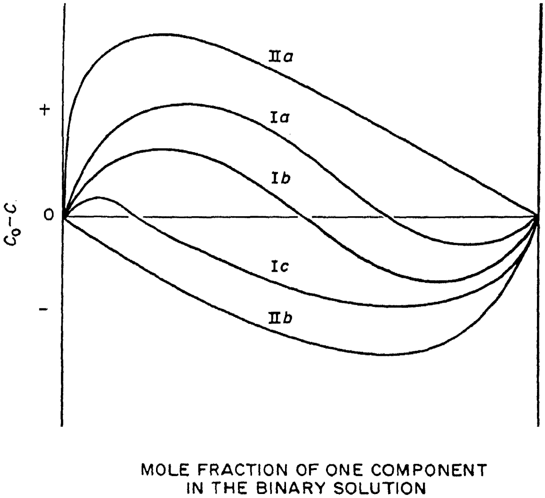

Fig. II-8. Diagrams of types of S-shaped isotherms. The apparent specific amount adsorbed is plotted against mole fraction of the component. c_0, original concentration; c, equilibrium concentration; v, volume of original solution; m, weight of adsorbent.

Another method of allowing for the simultaneous adsorption of solvent and solute was used by Wo. Ostwald and Izaguirre,[79] and also by Bartell and Sloan.[80] This is a method in which a theoretical equation is fitted to the data obtained over the entire concentration range for a binary solution. The fitting is accomplished by successive approximations.[80]

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[74] Jones and Outridge, *J. Chem. Soc.*, 1930, 1574.

[75] The method was also suggested by Patrick and Jones, *J. Phys. Chem.*, 29, 1 (1925), and used by Bakr and McBain, *J. Am. Chem. Soc.*, 46, 2718 (1924).

[76] Tryhorn and Wyatt, *Trans. Faraday Soc.*, 21, 399 (1925–26).

[77] Bachmann, *Z. anorg. Chem.*, 79, 202 (1913).

[78] Bakr and McBain, *J. Am. Chem. Soc.*, 46, 2718 (1924); K. S. G. Doss, *J. Chem. Soc.*, 1931, 2027; Doss, *J. Indian Chem. Soc.*, 14, 160 (1937).

[79] Wo. Ostwald and Izaguirre, *Kolloid-Z.*, 30, 279 (1922).

The types of data obtained when adsorption takes place on a solid adsorbent from a binary solution, studied over the entire range of concentration from 0 to 1 mole fraction, were gathered into eight classes by Ostwald and Izaguirre.[79] A simpler but not as precise classification will be used here. The data, when plotted according to the usual method (amount adsorbed against concentration of that component in mole fraction), may give for different systems curves which look different but which are to some extent variations on a single theme. These variations are shown schematically in Figure II-8. Different shapes support different interpretations of the mechanism of the adsorption.

Types II*a* and *b* are curves which would be obtained if one or the other component is so strongly adsorbed that to the extent permitted by its concentration it takes the surface of the adsorbent to the virtual exclusion of the other component. Curves of this type are less often observed, the more common curves being of Type I*a*, *b*, or *c*. Here, both solute and solvent are adsorbed.

It may indeed be that careful measurements will show that curves of Type II are not actually found, but that there is always some positive adsorption of the component present in the smaller amount in solution. However, Jones and Outridge[81] and Bartell and Scheffler[82] found curves for alcohols from benzene on silica gel which gave no negative selective adsorption of the alcohol. The method of plotting the data must be taken into account in comparing results of different workers.[83]

Wo. Ostwald and Izaguirre[84] derived equations for dealing with adsorption from a binary mixture over the entire concentration range on the basis of five possible behaviors. Let the components of the mixture be A and B, then: (*1*) component A alone may be adsorbed, and practically no B; (*2*) components A and B may both be adsorbed directly on the adsorbent; (*3*) B may not be adsorbed directly but may be brought into the interface through solvation of component A; (*4*) component B may be both directly adsorbed and brought into the interface by the solvated A; and (*5*) practically no A may be adsorbed, only B. Behaviors (*1*) and (*5*) are symmetrical and correspond to curves II*a* and II*b* in Fig. II-8, and (*2*) corresponds in general shape to curves of Type I. Only the derivation of the curves for behaviors (*1*) and (*2*) will be discussed here, though the others may be important for purposes of interpreting some data.

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[80] Bartell and Sloan, *J. Am. Chem. Soc.*, **51**, 1643 (1929).

[81] Jones and Outridge, *J. Chem. Soc.*, **1930**, 1574.

[82] Bartell and Scheffler, *J. Am. Chem. Soc.*, **53**, 2507 (1931).

[83] Gyani and Ganguly, *J. Phys. Chem.*, **49**, 226 (1945).

[84] Wo. Ostwald and Izaguirre, *Kolloid-Z.*, **30**, 279 (1922).

Let p = weight of component A (solute) and P that of B; N is the weight of the binary solution: $N = p + P$. The original concentration of component A in percent is $c_0 = 100\ p/N$. x is the actual weight of A adsorbed, and m the weight of the adsorbent. k, n, l, and a are constants.

In case (*1*), where component A alone is adsorbed, the original concentration of A as defined is:

$$c_0 = 100\ p/N \tag{15}$$

The equilibrium concentration will then be:

$$c = \frac{100(p - x)}{N - x} \tag{16}$$

and the difference:

$$c_0 - c = \frac{100p}{N} - \frac{100(p - x)}{N - x} = x\frac{100 - c}{N} \tag{17}$$

The specific adsorption of component A, x/m, is some function of the equilibrium concentration:

$$x/m = f(c)$$

If it is taken that this function is of the type:

$$x/m = kc^n \quad \text{(Freundlich equation)}$$

then, substituting for x, equation (17) becomes:

$$c_0 - c = kc^n(100 - c)(m/N) \tag{18}$$

Rewriting this equation to bring out the specific concentration difference, $(N/m)(c_0 - c)$, yields:

$$(N/m)(c_0 - c) = kc^n(100 - c) \tag{19}$$

Ostwald and Izaguirre point out that the specific concentration difference is independent of the absolute amount of adsorbent and solution in the given experiment. They feel that this equation (19) is preferable to the usual adsorption equation $x = mkc^n$ (an equation which they attribute to Boedeker).

This equation (19) always yields values greater than zero, since c is by definition positive and not greater than 100. The function shows a maximum when its first derivative is zero:

$$knc_{max.}^{n-1}\,(100 - c_{max.}) - kc_{max.}^{n} = 0$$

or

$$c_{max.} = (100\,n)/(n + 1)$$

and if n is less than 1, as it usually is, the maximum comes before $c = 50$; if n should be greater than 1, then a point of inflection becomes possible:

$$c \text{ inflection} = 100(n - 1)/(n + 1)$$

The point of inflection must be expected at a low concentration of component A.

In case (*2*), where both components A and B are adsorbed, the equation for the equilibrium concentration of component A must be changed to:

$$c = 100(p - x)/(N - x - W) \tag{20}$$

where W is the weight of B which is simultaneously adsorbed with A. Then:

$$c_0 - c = \frac{100p}{N} - \frac{100(p - x)}{N - x - W} \tag{21}$$

which can be rearranged to:

$$c_0 - c = x\,\frac{100 - c}{N} - \frac{Wc}{N} \tag{22}$$

Again, substituting for x by the relation $x = mkc^n$ as in case (*1*) and simplifying:

$$c_0 - c = \frac{m}{N}kc^n\,(100 - c) - \frac{W}{N}c \tag{23}$$

However W is not constant over all concentrations. It varies with B. Assuming a relation for W corresponding to that for x, namely:

$$W/m = l(100 - c)^{\alpha}$$

and substituting this in equation (23) one obtains:

$$c_0 - c = (m/N)kc^n(100 - c) - (m/N)l(100 - c)^{\alpha}(c) \tag{24}$$

which is rewritten to emphasize the specific concentration difference:

$$(N/m)(c_0 - c) = kc^n(100 - c) - l(100 - c)^{\alpha}(c) \tag{25}$$

This relation is positive at low values of c and negative at high values. The curve intersects the axis at some point between $c = 0$ and $c = 100$.

If α and n are less than 1 the curve will be S-shaped; if they are greater than 1 it will have two inflection points, one in the negative and one in the positive branch. A pair of the constants may be obtained provisionally from each branch of the curve: k and n from the dilute A side; and l and α from the dilute B portion, and then the final values obtained by approximation.

An equation identical to (25) was derived independently by Bartell and Sloan.[85] These authors found the Freundlich equation to apply to their data at low concentrations, and assuming that a similar function would apply to each component they derived the equation:

$$H\,\Delta x/m = ax^n(1 - x) - b(1 - x)^d x \tag{26}$$

in which H is total number of millimoles in solution, x mole fraction of component A at equilibrium, Δx the mole fraction change due to adsorption, m the weight of adsorbent, and a, n, b, and d constants. This equation is seen to be identical with that of Ostwald and Izaguirre for the same system. A discussion of some of this work is to be found in a paper by Heymann and Boye.[86]

Meeting this same problem, Rao[87] defined the selectivity of an absorbent thus:

$$s = w(c_i - c_1)/(m \times 100) \tag{27}$$

where w is the initial weight of liquid used in the experiment, c_i the initial and c_1 the final concentration in percent of component A_1, and m the weight of adsorbent. When selectivity (s) was plotted against equilibrium concentration of component A, (c_1), an S-shaped curve was obtained. If this equation is converted into the notation of Ostwald and Izaguirre, it becomes:

$$s = N(c_0 - c)/(m \times 100) \tag{28}$$

and it is evident that save for the difference in calculating percent or percent/100 the selectivity of Rao is Ostwald and Izaguirre's specific concentration difference (see Eq. 19).

Doss and Rao[88] have discussed these functions and methods of dealing with adsorption over the whole concentration range. The selectivity represents the weight of component A per gram of adsorbent in excess of the concentration in the equilibrium solution, the assumption being made that the number of grams of the mixture adsorbed does not change as the weight percentage of A in the absorptive changes from c_0 to c. Bartell's $H\Delta x/m$ is the number of millimoles of component A retained per gram of adsorbent in excess of the equilibrium concentration, the assumption being that the number of millimoles of material adsorbed does not change as the mole fraction of component A in it changes from x_0 to x. To correct for this assumption Doss and Rao write a corrected selectivity $s_{corr.}$:

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[85] Bartell and Sloan, *J. Am. Chem. Soc.*, 51, 1643 (1929).

[86] Heymann and Boye, *Kolloid-Z.*, 63, 154 (1933).

[87] B. S. Rao, *J. Phys. Chem.*, 36, 616 (1932).

[88] K. S. G. Doss and B. S. Rao, *Half-yearly J. Mysore Univ.*, 8, 49 (1935); see also M. R. A. Rao, *J. Indian Chem. Soc.*, 12, 345 (1935).

$$s_{corr.} = s_{obs.} + Vc(\rho_{ads.} - \rho_{sol.})/100 \tag{29}$$

where V is the volume of material adsorbed by a gram of adsorbent, c the equilibrium solution, $\rho_{ads.}$ the mean density of the material adsorbed, and $\rho_{sol.}$ the density of the equilibrium solution. A similar correction applied to Bartell's $H\Delta x/m$ yields:

$$(H\,\Delta x/m)_{corr.} = (H\,\Delta x/m)_{obs.} + Vx(\rho_{ads.,\,M} - \rho_{sol.,\,M}) \tag{30}$$

where $\rho_{ads.,\,M}$ and $\rho_{sol.,\,M}$ are the total number of millimoles present in 1 cc. of adsorbed material and of the equilibrium solution, respectively, and x is the mole fraction of the component A in the equilibrium solution. These corrected quantities bear the relation:

$$s_{corr.} = (H\,\Delta x/m_{corr.})(M_A/1000) \tag{31}$$

where M_A is the molecular weight of component A. In order to make these corrections the quantities ρ_{ads} or $\rho_{ads.,\,M}$ must be obtained. This can be done graphically[89] or by successive approximations.[90] The original papers should be consulted for the details.

V. MEASUREMENT OF THE CONTACT ANGLE

The magnitude of the angle of contact between two phases can, under proper conditions, give information about the extent of interaction of the phases. The measurement of the observed angle of contact is not difficult, but as Harkins has pointed out the discordance between the values given in the literature indicates the presence of more subtle difficulties than may often be realized.[91]

Contact angle may be measured in a number of ways.[92] Drops or bubbles may be made to rest on the surface to be examined. For example the contact angle at the vapor–liquid–solid interface may be examined by placing a drop of the liquid on the solid surface in an atmosphere saturated with the vapor of the system.[93] If the drop is formed from the tip of a tube it can be made to increase in size, or decrease, and the "advancing" and "receding" contact angles measured. In another method the solid is immersed in the liquid, plane side downward, and a bubble of the vapor is formed so that it rests against this surface.[94] The bubble can be made to grow or shrink by manipulating the pressure of the gas. In this way advancing and receding angles can be investigated. Similar methods can be applied to angles measured between two liquids and a solid, the solid being immersed in the one liquid and a drop of the other being formed against the solid surface. If the solid rests in the less dense liquid the more dense can be dropped on it; if in the more dense liquid, the other can be brought up under the solid surface.

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[89] K. S. G. Doss, *J. Chem. Soc.,* 1931, 2027.

[90] Jones and Outridge, *J. Chem. Soc.,* 1930, 1574.

[91] Harkins, *J. Chem. Phys.,* 9, 552 (1941).

[92] N. K. Adam, *The Physics and Chemistry of Surfaces.* 3rd ed., Oxford Univ. Press, London, 1941.

An elegant method of determining the contact angle was contrived by Adam and Jessop.[95] The solid in the form of a plate is dipped through the interface formed by the other two phases, so that the three phases meet in a line and then the plate is tilted until the liquid meets the plate at a clean line. The angle of tilt of the plate can then be measured. Advancing and receding angles can be obtained by moving the plate downward or upward in the surface at a constant tilt. The tilted plate method has found considerable use.[96] The principle has been applied to measure the wetting of wires, or fibers.[97]

Other methods may also be mentioned. Wetting can be determined by capillary rise and by a vertical rod method.[98] When the wetting of powders has to be measured the "pressure of displacement" method of Bartell and coworkers[99] may be used. Contact angles may be measured between a lens of liquid floating on another liquid.[100] Some of these methods are quite old.[101] The subject is one which cannot be dealt with further here.[102]

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[93] Bartell and Bristol, *J. Phys. Chem.*, 44, 86 (1940).

[94] Mack and D. A. Lee, *J. Phys. Chem.*, 40, 169 (1936).

[95] Adam and Jessop, *J. Chem. Soc.*, 1925, 1863; also Adam and Morrell, *J. Soc. Chem. Ind.*, 53, 255T (1934).

[96] Fowkes and Harkins, *J. Am. Chem. Soc.*, 62, 3377 (1940).

[97] Adam, *J. Soc. Dyers Colourists*, 53, 121 (1937).

[98] Bartell, Culbertson, and Miller, *J. Phys. Chem.*, 40, 881 (1936).

[99] Bartell and Osterhof, *Colloid Symposium, Monograph*, 4, 234 (1926); 5, 113 (1927); *Ind. Eng. Chem.*, 19, 1277 (1927).

[100] N. F. Miller, *J. Phys. Chem.*, 45, 1025 (1941).

[101] N. K. Adam, *The Physics and Chemistry of Surfaces*. 3rd ed., Oxford Univ. Press, London, 1941.

[102] See ref. 101, and A. M. Schwartz and J. W. Perry, *Surface Active Agents*, Interscience, New York, 1949; A. E. Alexander and P. Johnson, *Colloid Science*, Oxford Univ. Press, London, 1949.

CHAPTER III

Relations between Relative Adsorbability and Properties of Phases

I. INTRODUCTION

A most important property influencing the nature of a solution is the solubility of the solute, the inverse of the escaping tendency of the adsorptive molecules from the solution. This will be discussed, with the usual classification into effects observed at liquid–vapor, liquid–solid, and liquid–liquid interfaces. Other properties of the phases will be given some attention. Many of these properties are related to and affect solubility. Throughout the discussion relative values will be compared, since it will usually be difficult to obtain quantitative correlations.

II. RELATION BETWEEN SOLUBILITY AND ADSORBABILITY

Langmuir,[1] Hildebrand,[2] and many others have pointed out that the solubility of a substance in a given solvent may be expected to affect its adsorbability. The solubility of one substance in another depends upon the readiness with which the two molecular species can mix. Ideal behavior in this respect is shown by relatively few substances. The components of such systems are usually quite similar in physical and chemical properties so that the intermolecular forces acting upon the molecules of one component are not greatly affected by the presence of the second.

Deviations from ideal behavior are usually ascribed to one or more of three causes: association of solute or solvent, solvation of one component by another, or dissociation of one or more components. Where solvation occurs the solution behaves as though it were more concentrated than might be calculated from the stoichiometric composition on the basis of ideal behavior. This is because solvent molecules are tied up by solute. Also, in such cases solutes show a greater solubility than might be expected from such properties of the pure solute as heat of fusion and melting point. (If the solvation union is strong enough to form a new chemical compound the resulting product may be more or less soluble.

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[1] Langmuir, *J. Am. Chem. Soc.*, 39, 1848 (1917).

[2] J. H. Hildebrand, *Solubility of Non-electrolytes*. 2nd ed., Reinhold, New York, 1936.

Such cases of compound formation are excluded here.) Association of the solute makes the solution seem less concentrated to tests which measure the number of particles present. Association of solute may increase solubility. For example, acetic acid dissolved in benzene is present largely as the dimer, which, due to chelation at the carboxylic acid group, is less polar than the monomeric acid. The depolarization that comes with dimerization would be expected to increase the solubility in the nonpolar solvent. Association of solvent, on the other hand, would be expected to operate against the otherwise expected solubility of the solute. Dissociation of solute or solvent may increase the number of particles in the solution over the number expected of an ideal undissociated solution.

Extreme deviation from ideal behavior can be regarded as a consequence of dissimilarity of the components of the solution.[2] Components which are unlike each other are usually also not very soluble in each other. If accumulation in an interface is considered as a manifestation of the escaping tendency of the adsorptive from the solution phase, then less soluble substances should tend to be adsorbed to a greater extent than more soluble ones. If the distribution aspect of adsorption is taken as the basis for prediction it would follow that more soluble substances would tend less to enter the interfacial phase than less soluble ones.[3]

When extent of adsorption *at the surface of a solution* and relative solubility in the solution are compared for two adsorptives, rather good correlation might be expected, because the properties of the interface will be largely controlled by the liquid phase. The correlation would be expected to be particularly good if homologous solutes were compared; it would be especially good with closely related isomers. In comparing the relative adsorptions at the surfaces and the solubilities of an adsorptive in different solvents, it might again be expected that reasonably good correlation would be found, particularly if the two solvents were homologous, or of the same solvent type.

When solubility is compared with extent of adsorption at a *solution–solid interface* there is present a variable, the solid surface, which neither controls nor is related to the solubility of the adsorptive. Correlations between solubility and adsorption onto a solid surface should not then be expected except in those cases in which the adsorbent does not play a powerful role in the process. With these general classifications in mind it is possible to gather enough data to test whether there is a correlation between solubility and adsorption.

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[3] L. C. Craig and D. Craig, "Extraction and Distribution," in Weissberger, ed., *Technique of Organic Chemistry,* Vol. III, Interscience, New York, 1950, p. 171 ff.

1. Solution–Vapor Interface

A. PAIRS OF LIQUIDS

The relation between extent of adsorption and miscibility in a binary mixture has been tested by examining the change in surface tension with concentration over the entire concentration range and comparing it with the change in vapor pressure.[4] One set of results is shown in Figure III-1. The results reveal a marked relationship between surface tensions and vapor pressures of mixed liquids. The relationship was summarized by Worley in three rules:

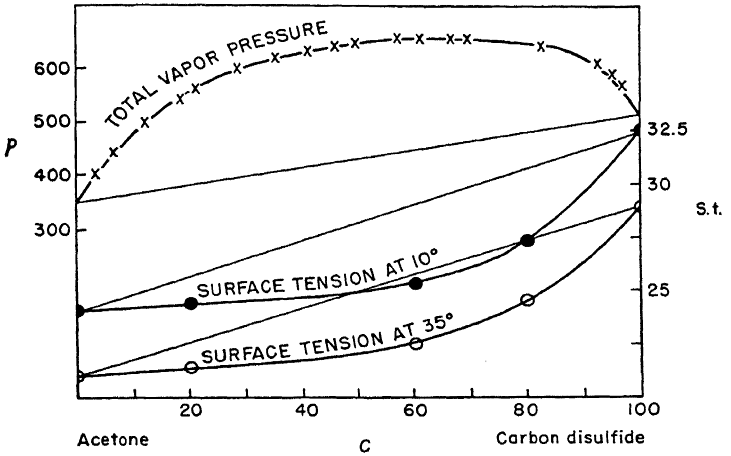

Fig. III-1. Comparison of vapor pressure–composition curve and surface tension–composition curves for the system acetone–carbon disulfide. *Upper curve:* vapor pressure (p) in millimeters of mercury at 35.17°; composition (C) in mole percent.[5] *Lower curves:* surface tension (S.t.) in dynes/cm. at 10 and 35°; composition (C) in volume percent.[6] The straight lines represent the ideal relation.

(*1*) If at any given temperature the vapor pressures of mixtures of two liquids agree with values calculated by the rule of admixture in molecular proportions, then at that temperature the surface tensions of the mixtures agree with those calculated by the formula $S = V_1S_1 + V_2S_2$ (where V_1 and V_2 are the volumes of the liquids in the mixture expressed fractionally, and S_1 and S_2 their surface tensions when unmixed).

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[4] Worley, *J. Chem. Soc.*, 1914, 273.

[5] Plotted from von Zawidski, *Z. physik. Chem.*, 35, 129 (1900); Table 28, pp. 154–155.

[6] Plotted from Worley, *J. Chem. Soc.*, 1914, 273; Table 12, p. 277.

(*2*) If the vapor pressures are greater than those calculated, then the surface tensions are less than those calculated.

(*3*) If the vapor pressures are less than those calculated, then the surface tensions are greater than those calculated. Mixtures may obey the admixture rule at one temperature and not at other temperatures.

These findings can be correlated with the general statements of Hildebrand.[7a] In discussing deviations from Raoult's law he states,[7b] in connection with the solubilities of gases and solids, that a positive deviation from Raoult's law corresponds to a smaller solubility, and a negative deviation to a greater solubility than would be calculated in the case of gases from the Clausius-Clapeyron equation, and for solids from the melting point and the heat of fusion. He also summarizes a discussion of the Gibbs equation with the statement[7c] that adsorption of a solute at a surface is favored by positive deviations from Raoult's law. Exceptions to the correlation have been observed.[8]

B. HOMOLOGOUS ADSORPTIVES

When the adsorption of homologs from aqueous solutions is compared at equivalent molar concentrations, or over equal ranges, it is observed that the adsorption increases (surface tension falls) in a quite regular manner with increase in molecular weight. Duclaux[9] investigated the concentrations of pairs of homologs which would give the same surface tension lowering in water. He found that for a given surface tension lowering the ratios of the concentrations of one homolog to another yielded for each pair a constant which was independent of the value of surface tension at which the comparison was made. That is, if the equation for the surface tension – concentration curve of a given homolog were $x = f(y)$ then the equation for the other homolog would be $x = kf(y)$. He found no relation between k and the equivalent weights of the substances. The order of surface activity found by Duclaux was methyl alcohol < ethyl < amyl alcohol; and formic acid < acetic < butyric acid.

Traube[10] observed this regular change in surface activity along an homologous series. In earlier work[11] he pointed out a qualitative correlation between solubility and capillary activity; the ability of a substance to lower surface tension was greater the less its solubility in water. This correlation held for several cases: for esters; for propionaldehyde com-

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[7] (*a*) J. H. Hildebrand, *Solubility of Non-electrolytes*. 2nd ed., Reinhold, New York, 1936. (*b*) *Ibid.*, p. 55. (*c*) *Ibid.*, p.190.

[8] Belton and Evans, *Trans. Faraday Soc.*, 41, 1 (1945).

[9] Duclaux, *Ann. chim. phys.* (5), 13, 76 (1878).

[10] Traube, *Ann.*, 265, 27 (1891).

[11] Traube, *Ber.*, 17, 2294 (1884).

pared with acetone; for butyric and isobutyric acids; for normal, iso, and tertiary butyl alcohols; for isoamyl alcohol, and 2-methyl-2-butanol. The implications of this regularity were discussed by Langmuir,[12] who showed how in distributing molecules between the solution and the surface the work done shows a constant value per CH_2 group in the molecule. This matter was examined by Ward[13] and is discussed in Chapter 1. There is evident, then, in some instances, an inverse relation between relative adsorbabilities and solubilities. Whereas the extent of adsorption on the surface of aqueous solutions at given concentrations increases steadily with number of CH_2 groups for the lower members of the homologous series of fatty acids, alcohols, esters, ethers, etc., this is just the order in which solubility decreases. Pertinent data for the fatty acids are given in Table III-1. Capillary activities of alcohols in aqueous solutions, as given by Weber and Sternglanz,[14] are summarized in Table III-2. There is an inverse relationship between the adsorptions of these homologs and their solubility in water. Other studies of this kind could be cited.[15]

TABLE III-1

Extent of Adsorption as Measured by Fall in Potential Energy Compared with Solubility for Fatty Acids

Fatty acid	Fall in potential energy on adsorption, erg $\times 10^{-14}$ [a]	Solubility in water, g. acid per 100 g. water[b]
Butyric (C_4)	41.5	
Valeric (C_5)	45.1	
Caproic (C_6)	48.3	0.968
Heptoic (C_7)	52.1	0.244
Caprylic (C_8)	56.5	0.068
Pelargonic (C_9)	60.3	0.026
Capric (C_{10})	65.0	0.015

[a] Ward, *Trans. Faraday Soc.*, 42, 399 (1946), Table II, p. 404.
[b] Ralston and Hoerr, *J. Org. Chem.*, 7, 546 (1942).

There exists, however, the exception of the dibasic acids. Tamamushi[16] reported the order of capillary activity to be oxalic < succinic < glutaric < adipic. The order of solubility is adipic < pimelic < succinic < oxalic < glutaric < malonic. The only semblance of order here is found[16] with the acids with even numbers of carbon atoms. Exceptions may also occur when somewhat unlike substances are compared.

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[12] Langmuir, *J. Am. Chem. Soc.*, 39, 1848 (1917).

[13] Ward, *Trans. Faraday Soc.*, 42, 399 (1946).

[14] Weber and Sternglanz, *Z. physik. Chem.*, A169, 241 (1934).

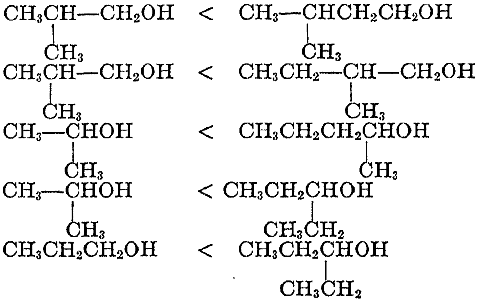
[15] Szyszkowski, *Z. physik. Chem.*, 64, 385 (1908). Weigner, Magasanik, and Virtanen, *Kolloid-Z.*, 28, 51 (1921). King, Kansas Agr. Expt. Sta., *Tech. Bull.* 9, 1922.

[16] Tamamushi, *Bull. Chem. Soc. Japan,* 7, 168 (1932).

Turning to nonaqueous solvents, slight adsorption of long-chain fatty acids at the surface of a high-molecular hydrocarbon oil was reported by Gilbert.[17] Wöhler and Wenzel[18] found the surface tension of pentane little altered by the adsorption of paraffin. This is understandable in that the solvent and solute here are so much alike in chemical nature.

TABLE III-2

Comparison of Capillary Activity of Some Branched Homologous Alcohols in Water



Relative capillary activity[a]		
$CH_3CH(CH_3){-}CH_2OH$	<	$CH_3{-}CH(CH_3)CH_2CH_2OH$
$CH_3CH(CH_3){-}CH_2OH$	<	$CH_3CH_2{-}CH(CH_3){-}CH_2OH$
$CH_3{-}CH(CH_3)OH$	<	$CH_3CH_2CH_2CH(CH_3)OH$
$CH_3{-}CH(CH_3)OH$	<	$CH_3CH_2CH(CH_2CH_3)OH$
$CH_3CH_2CH_2OH$	<	$CH_3CH_2CH(CH_2CH_3)OH$

[a] Data from Weber and Sternglanz, *Z. physik. Chem.*, A169, 241 (1934).

C. ALTERED SOLUBILITIES

The relation between solubility and surface tension lowering (extent of adsorption) can be made by comparing different solvents through a given adsorptive. This has been done either by using chemically different solvents, or by altering the solvent power of a given solvent through changing its temperature or by admixture of other substances.

Alteration of Solubility by Temperature Change. Worley[19] made substances more soluble by raising the temperature, and examined the correlation between solubility and surface tension lowering. One set of results is shown in Figure III-2. He concluded that in the cases of aniline–water (Fig. III-2) and phenol–water, in which increase in temperature increased the solubility, the surface tension became less abnormal and tended to approach the value it might be expected to have if the liquids were miscible in all proportions. No such tendency was found in the system isobutyl alcohol – water, in which solubility was little affected by temperature over the range examined. This behavior occurs because the surface layer, because of adsorption, is always nearer to saturation than the bulk phase, and if solubility increases with rise in temperature the surface layer becomes less nearly saturated with rise in temperature. Worley suggested, further, that in some cases the bulk concentration may even become greater at the expense of the surface concentration.

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[17] Gilbert, *J. Phys. Chem.*, 31, 543 (1927).

[18] Wöhler and Wenzel, *Kolloid-Z.*, 53, 273 (1930).

[19] Worley, *J. Chem. Soc.*, 1914, 260.

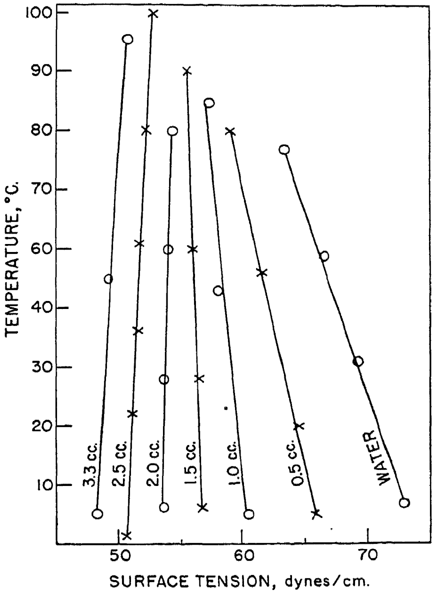

Fig. III-2. Influence of temperature on the surface tensions of mixtures of aniline in water.[19] Each point is the mean of four observations. The figures on the curves indicate the amounts of aniline added to 100 cc. of water.

Rehbinder[20] examined the relation between surface activity and concentration for aqueous solutions of fatty acids from C_3 to C_7 over a range from 0 to 100°C. The Traube order held at the different temperatures. The relationship of the surface tension – concentration curves of two neighboring homologs changed with temperature. With increase in temperature the surface tension decreased, and the curves became less curved. In the capillarity–temperature diagram some curves showed a maximum. This usually lay between 10 and 40°.

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[20] Rehbinder, *Z. physik. Chem.*, 111, 447 (1924).

Alteration of Solubility by Admixture. Solvent power may be altered by admixture. The third substance may decrease, increase, or leave virtually unchanged the solubility of the adsorptive. Weigner, Magasanik, and Virtanen[21] found that for lower fatty acids in water the order of increasing surface tension lowering is acetic, propionic, butyric. The same order was observed for the acids in 2 N sodium chloride solutions, but there was increased lowering with increase in salt concentration and the effect of the addition of salt increased within the homologous series from acetic to butyric. Adsorption of acetone and of ethanol also was increased by the presence of sodium chloride (2 N solution). The authors pointed out that the addition of strong electrolytes to water affects the solution by tying up water molecules. This causes the effective concentration of the other solute to be greater, and so accounts for the observed effects. As regards a correlation with solubility it may be mentioned only that the addition of inorganic salts to water usually tends to salt out

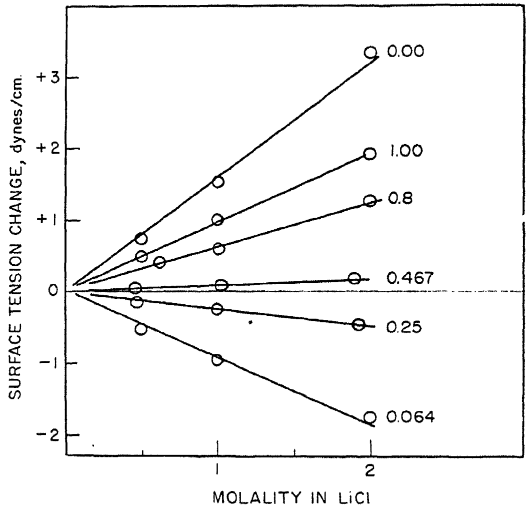

Fig. III-3. Surface tension changes produced by lithium chloride in water–alcohol solutions.[23] Figures on the curves indicate mole fraction of alcohol.

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[21] Weigner, Magasanik, and Virtanen, *Kolloid-Z.*, 28, 51 (1921).

organic solutes. There is evidence, then, that an adsorptive can be driven into the surface of a solution by decreasing the solvent power of the medium through admixture of a suitable salt.[22]

The adsorption of alcohol and of water at the surface of water – alcohol – lithium chloride solutions was calculated by Butler and Lees[23] from measurements of surface tension, from data on partial pressures of water and alcohol for the system,[24] and on the assumption that no lithium chloride was adsorbed. The data on surface tension change are plotted in Figure III-3. Increase in salt caused an increase in surface tension of the pure solvents. In the water–alcohol mixture, surface tension lowering reached a maximum in dilute solution where the activity of the alcohol was increased (as judged from vapor-pressure curves) by the salting-out effect of the lithium chloride; however, in the concentrated alcohol solutions the salt was solvated with alcohol and here the activity of the alcohol was lowered. The activity of the water was lowered by the salt at all concentrations of alcohol and salt.

The "salting out" of a solute by another solute is a common phenomenon. It has been observed, on the other hand, that substances may be "salted in" to a solution, provided a suitable salt is used. Whereas the addition of sodium chloride to isobutyric acid in water causes the two to be less miscible, the addition of potassium isobutyrate to aqueous isobutyric acid improves the miscibility of the acid and the water.[25] Bury and Mends[25] point out that this increase in solubility brought about by potassium isobutyrate is greater than would be expected on the hypothesis of complex formation because, in the case of small additions of potassium isobutyrate, about eight molecules of isobutyric acid enter the water for each molecule of salt. Complicated behaviors of this type can occur when some of the particles involved are of colloidal dimensions.[26] The phenomenon also has implications in extraction.[27] Hartley[28] has explained the salting-in behavior as caused by micelle formation. The substances that are solubilized dissolve in these micelles, or, if amphipathic, may be oriented, and contribute to the micelle.[29] Other interpretations have been given for the phenomenon.[30] The subject has been reviewed by Hartley.[31] Increasing of solvent power by salting in should decrease adsorption for much the same reason that complex formation would. If it decreases the concentration of free adsorptive molecules in the bulk phase, the extent of adsorption should be decreased. The possible adsorption of the micelles themselves, however, should not be overlooked.

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[22] Worley, *J. Chem. Soc.*, 1914, 260. Berczeller, *Biochem. Z.*, 66, 173 (1914).

[23] Butler and Lees, *J. Chem. Soc.*, 1932, 2097.

[24] Shaw and Butler, *Proc. Roy. Soc., London,* A129, 519 (1930).

[25] Bury and Mends, *J. Chem. Soc.*, 1939, 742.

[26] Angelescu and Popescu, *Kolloid-Z.*, 51, 247, 336 (1930). Wo. Ostwald and Izaguirre, *ibid.*, 32, 57 (1923). Walker, *J. Chem. Soc.*, 1921, 1521.

[27] L. C. Craig and D. Craig, "Extraction and Distribution," in Weissberger, ed., *Technique of Organic Chemistry,* Vol. III, Interscience, New York, 1950, p. 171 ff.

[28] Hartley, *J. Chem. Soc.*, 1938, 1968; and other papers listed there.

[29] Hartley, in *Wetting and Detergency.* Harvey, London, 1937, p. 153.

A third possibility is that the addition of another solute may have little or no effect upon the surface tension of the solution. Von Szyszkowski[32] showed that, when aqueous solutions of two substances which are chemically much alike and which are at concentrations with the same surface tensions are mixed, the solution which results shows the same surface tension as the two solutions that were mixed. For example, 0.581 N isobutyric acid has the same surface tension as 0.199 N isovaleric acid. Whether these solutions were mixed in the ratios 1:1, 1:2, or 1:3, the final mixture showed the same surface tension as the original solutions. This author[32] showed, moreover, that a mixed solution of this kind gives on dilution the same surface tension curve as a solution mixed in another ratio, indicating that the course of the dilution curve is independent of the ratio in which the two solutions of equal surface tension were mixed. When two solutions of different surface tension were mixed the surface tension of the mixture fell between the two, and could be calculated from the concentration of the mixture. The dilution curve in such a mixture followed the predicted course quite closely. When two acids such as isobutyric and isocaproic, which have surface tension – concentration curves of different shapes, were mixed, even with both solutions initially of the same surface tension, the mixture showed a surface tension value different from that of the components due to the unlike change with dilution. However, additivity of the capillary properties of the two acids was still found; the dilution curve of the mixture lay between the curves of the components and approached that of the major component.

2. Solution–Solid Interface

The solubility of a substance is a matter between it and the solvent and is not under the control of any insoluble third substance that may be present. But whereas a third substance, such as a solid adsorbent, may control the conditions at the solution – solid interface, no *general* correlation between adsorption at this interface and solubility in the solvent can be expected.

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[30] McBain and Woo, *J. Am. Chem. Soc.*, 60, 223 (1938); and the papers cited there.

[31] Hartley, *Ann. Reports*, 45, 33 (1949); also, A. M. Schwartz and J. W. Perry, *Surface Active Agents*, Interscience, New York, 1949.

[32] Szyszkowski, *Z. physik. Chem.*, 64, 385 (1908).

An inverse relationship between solubility and adsorbability was suggested by Lundelius[33] on the basis of measurements of the adsorption of iodine from chloroform, carbon tetrachloride, and carbon bisulfide onto an acid-purified blood charcoal. Lundelius derived the relation that in the adsorption equation $x/m = kC^n$ (Chapter II) the constant k was inversely proportional to the nth power of the solubility of the adsorptive in the solvent in question. The idea that there should be some relationship between extent of adsorption and solubility has been a very persistent one,[34] and has indeed received some experimental support. However the quantitative relation of Lundelius has been found to have only restricted applicability.[35] The relation has been investigated by comparing binary mixtures, homologs, isomers, chemically different substances, solvents, etc. A few examples are given below, chiefly in tables and figures.

A. ADSORPTION FOR BINARY MIXTURES

The measurement of adsorption over the entire concentration range for binary mixtures and the interpretations of the results have already been dealt with (Chapter II). In Table III-3 are summarized data on measurements of adsorption from binary mixtures onto a number of adsorbents. The effects of phases seem to be evident from these data. Thus, when a given charcoal is used (Table III-3) benzene is somewhat better adsorbed from hexane than is nitrobenzene; but, from the binary mixture, nitrobenzene is somewhat better adsorbed than benzene. In another cross-comparison, methyl alcohol is a little better adsorbed than carbon tetrachloride; carbon tetrachloride is much better adsorbed than amyl alcohol; methyl alcohol is found to be much better adsorbed than amyl alcohol. With two different charcoals the adsorptions may be reversed: in one case carbon tetrachoride is better adsorbed than benzene; in the other the reverse is true. With the same charcoal activated in different ways the adsorption order can be reversed.

In general, from these binary mixtures, substances of an aromatic nature are better adsorbed on charcoals than polar substances, but the nature of the charcoal influences the extent of the adsorption. In many cases it is difficult to draw conclusions. In adsorption onto the very polar silica gel, the polarizable benzene is better adsorbed than the less polarizable heptane; the benzene is as well adsorbed as carbon tetrachloride, and less well

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[33] Lundelius, *Kolloid-Z.*, 26, 145 (1920).

[34] Georgievics, *Kolloid-Z.*, 28, 253 (1921).

[35] Angelescu and Comanescu, *Kolloid-Z.*, 44, 288 (1928). Sata, *ibid.*, 49, 275 (1929).

TABLE III-3

Relative Adsorbabilities of the Components of Binary Mixtures on Solid Adsorbents

Adsorbent	Relative order of adsorbability of the two components, and mole fraction of the more strongly adsorbed at which the isotherm cuts the concentration axis (see Fig. II-8). 1.0 means that preferential adsorption occurred over the entire range	
Charcoal	α-bromonaphthalene < benzene[b]	0.55
	benzene < nitrobenzene at 20°[f]	0.65
	benzene < nitrobenzene at 100°[f]	0.71
	hexane < nitrobenzene[f]	0.775
	carbon tetrachloride < benzene[f]	0.8
	hexane < benzene[f]	0.87
	cyclohexane < benzene[f]	0.9
Norit	benzene < carbon tetrachloride[r]	1.0
150° charcoal	benzene < ethyl alcohol[m]	0.575–0.61
400° charcoal	ethyl alcohol < benzene[m]	0.63–0.685
1000° charcoal	ethyl alcohol < benzene[m]	0.79–0.875
Blood charcoal	ethyl alcohol < benzene[o]	0.75
(H_2, CO_2) charcoal	ethyl alcohol < benzene[o]	0.8
	ethyl alcohol < benzene[o]	1.0
Charcoal	methyl alcohol < benzene[l]	0.75
	ethyl alcohol < benzene[b]	0.8
	ethyl alcohol < benzene[f]	0.8–0.9
	propyl alcohol < benzene[l]	0.925
	butyl alcohol < benzene[l]	0.925
	isoamyl alcohol < benzene[l]	1.0
Norit	ethyl alcohol < benzene[o]	1.0
	isoamyl alcohol < benzene[p]	1.0
Charcoal	ethyl carbonate < benzene[b]	0.99
	ethyl alcohol < nitrobenzene[f]	0.83
	ethyl alcohol < ethyl carbonate[b]	0.55
	ethyl carbonate < α-bromonaphthalene[b]	*ca.* 0.8
	carbon tetrachloride < methyl alcohol[f]	0.52
	ethyl alcohol < carbon tetrachloride[f]	0.65
	butyl alcohol < carbon tetrachloride[f]	0.70
	amyl alcohol < carbon tetrachloride[f]	0.85
Norit	amyl alcohol < carbon tetrachloride[q]	0.8
Charcoal	amyl alcohol < methyl alcohol[f]	0.76
	water < ethyl alcohol[f]	1.0
	acetic acid < carbon disulfide[f]	0.56
Blood charcoal	acetic acid < benzene[s]	0.6
Sugar charcoal	acetic acid < benzene[s]	0.75
Charcoal	acetic acid < ethyl bromide[a]	0.84
Blood charcoal	water < acetic acid[n]	—
Charcoal	water < butyric acid[f]	0.72
Silica gel	carbon tetrachloride ≥ benzene[r]	0.5
	benzene < ethyl carbonate[d]	0.68
	heptane < benzene (at. 30, 74, 98°)[i]	1.0
	isoamyl alcohol < benzene[p]	0.65

Table continued

Adsorbent	Relative order of adsorbability of the two components, and mole fraction of the more strongly adsorbed at which the isotherm cuts the concentration axis (see Fig. II-8). 1.0 means that preferential adsorption occurred over the entire range	
Silica gel	benzene < isoamyl alcohol[e]	0.73
	benzene < *n*-butyl alcohol[e]	0.82
	benzene < ethyl alcohol[d]	0.85
	benzene < *n*-propyl alcohol[e]	0.86
	benzene < ethyl alcohol[e]	0.86
	benzene < ethyl alcohol[o]	0.9
	benzene < ethyl alcohol[g,h,i]	1.0
	benzene < methyl alcohol[e]	1.0
	benzene < *n*-butyl alcohol[c]	1.0
	isoamyl alcohol < carbon tetrachloride[q]	0.8
	carbon tetrachloride < ethyl alcohol[h,j]	1.0
	methyl benzoate < ethyl carbonate[d]	0.9
	water < acetone[j]	0.755
	dimethylaniline < ethyl carbonate[d]	0.92
	water < pyridine[i,j]	0.78 (wt. %)
	alcohol < pyridine[l]	0.785 (wt. %)
	heptane < pyridine[h]	1.0
	benzene < acetic acid[s]	1.0
Alumina	benzene < carbon tetrachloride[k]	0.64 (wt. %)
	benzene < ethyl alcohol[k]	1.0
	carbon tetrachloride < ethyl alcohol[k]	1.0
	ethyl alcohol < water[k]	1.0
	pyridine < water[k]	1.0
Ferric oxide gel	carbon tetrachloride < benzene[k]	1.0
	benzene < ethyl alcohol[k]	1.0
	carbon tetrachloride < ethyl alcohol[k]	1.0
	ethyl alcohol < water[k]	1.0
	pyridine < water[k]	1.0

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[a] Wo. Ostwald and Schulze, *Kolloid-Z.*, **36**, 289 (1925); dry charcoal.

[b] Bartell and Sloan, *J. Am. Chem. Soc.*, **51**, 1643 (1929); purified charcoal.

[c] Jones and Outridge, *J. Chem. Soc.*, **1930**, 1574.

[d] Bartell, Scheffler, and Sloan, *J. Am. Chem. Soc.*, **53**, 2501 (1931); silica gel.

[e] Bartell and Scheffler, *J. Am. Chem. Soc.*, **53**, 2507 (1931); silica gel; purified charcoal.

[f] Heymann and Boye, *Kolloid-Z.*, **63**, 154 (1933); dry ash-free wood charcoal.

[g] M. R. A. Rao, *J. Indian Chem. Soc.*, **12**, 326 (1935); silica gel in which water was replaced by HCl (contained no water, but *ca.* 10% HCl by wt.). Vapor phase adsorption.

[h] M. R. A. Rao, *ibid.*, **12**, 345 (1935); silica gel, Patrick's, and another gel.

[i] M. R. A. Rao, *ibid.*, **12**, 371 (1935); Patrick's silica gel.

[j] K. S. G. Doss and B. S. Rao, *Half-yearly J. Mysore Univ.*, **8**, 49 (1935–36); silica gel prepared by Rao and Doss, *J. Phys. Chem.*, **35**, 3486 (1931).

[k] K. S. Rao and B. S. Rao, *Proc. Indian Acad. Sci.*, **A4**, 562 (1936).

[l] Venkatanarasimhachar and K. S. G. Doss, *ibid.*, **A6**, 32 (1937).

[m] Bartell and Lloyd, *J. Am. Chem. Soc.*, **60**, 2120 (1938); purified charcoal activated in oxygen at various temperatures.

[n] Dobine, *Compt. rend.*, **212**, 155 (1941); blood charcoal.

[o] N. S. Rao and S. K. K. Jatkar, *Quart. J. Indian Inst. Sci.*, **5**, 73 (1942); Norit and blood charcoal, commercial products; sugar charcoal; silica gel from nickel silicate, purified with HCl.

[p] Rao and Jatkar, *ibid.*, **5**, 80 (1942).

[q] Rao and Jatkar, *ibid.*, **5**, 87 (1942).

[r] Rao and Jatkar, *ibid.*, **5**, 91 (1942).

[s] Rao and Jatkar, *ibid.*, **5**, 98 (1942).

adsorbed than the alcohols, esters, and other polar substances. These comparisons, as summarized in III-3, are the types of data which, in the absence of direct tests, might furnish a basis for judging eluent powers of solvents (Chapter V) for chromatographic purposes.

B. ADSORPTION OF HOMOLOGS FROM A GIVEN SOLVENT TO A GIVEN ADSORBENT

Perhaps the most extensive study of this kind has been made by Linner and Gortner.[36] These authors studied the adsorption of thirty-one organic acids from water solution onto Norit decolorizing charcoal. The order of increasing adsorption for the fatty acids was formic, acetic, propionic, butyric, valeric, caproic (see Fig. IV-1). This is the order of decreasing solubility. Similar data, but not on such an extensive series of acids, have been reported by Bhatnagar *et al.*[37] for adsorption on *n*-phenylenediamine-formaldehyde resin from water, and by Weigner, Magasanik, and Virtanen[38] for adsorption on blood charcoal from water. Correlation with relative solubility was not clear for the dicarboxylic acids because the curves of amount adsorbed *vs.* concentration crossed in some cases.

Amiot[39] reported the order of adsorption on charcoal from aqueous solution as ethanol $<$ butanol. This is the reverse of the solubility order.

C. ADSORPTION OF ISOMERS

When the relative extents of adsorption of isomers from the same solvent to a given absorbent are compared with relative solubility, data of the type shown in Table III-4 are obtained.

D. ADSORPTION OF SUBSTANCES NOT ISOMERS OR HOMOLOGS

Table III-5 contains comparisons of relative adsorptions and solubilities of a number of different substances adsorbed from a given solvent to the same adsorbent in each case.

E. EFFECT OF TEMPERATURE

Wöhler and Wenzel[40] adsorbed acetic, propionic, butyric, and valeric acids on Merck *carbo animalis* from aqueous solution. They found that

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[36] Linner and Gortner, *J. Phys. Chem.,* 39, 35 (1935).

[37] S. S. Bhatnagar, Kapur, and M. S. Bhatnagar, *J. Indian Chem. Soc.,* 16, 249 (1939).

[38] Weigner, Magasanik, and Virtanen, *Kolloid-Z.,* 28, 51 (1921).

[39] Amiot, *Compt. rend.,* 208, 1575 (1939).

[40] Wöhler and Wenzel, *Kolloid-Z.,* 53, 273 (1930).

TABLE III-4

Comparison of Solubilities and Extents of Adsorption of Isomers

Relative extents of adsorption	Relative solubilities in water
Isobutyric acid < *n*-butyric[a]	>
Isovaleric acid < *n*-valeric[a]	>
Maleic acid < fumaric[a]	>>>
Citraconic acid (methyl maleic) < mesaconic (methyl fumaric)[a,c]	>>>
Cyclohexanedicarboxylic acids[b]	
ortho: *trans* < *cis*	*trans* < *cis*
meta: *cis* < *trans*	*cis* > *trans*
para: *cis* < *trans*	*cis* > *trans*
Hydroxybenzoic acids:[c]	
para < *meta* < *ortho*	*p* > *m* > *o*

[a] Data from Linner and Gortner, *J. Phys. Chem.*, **39**, 35 (1935), for adsorption from water onto Norite charcoal.

[b] Data from Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 70 (1928), for adsorption from water on alcohol-extracted Merck *carbo medicinalis*, containing 10% moisture and 5.9% ash.

[c] Data from Sata, *Kolloid-Z.*, **49**, 275 (1929), for adsorption on Merck animal charcoal from water.

TABLE III-5

Comparison of Solubilities and Extents of Adsorption of Substances of Different Chemical Types[a]

Relative extents of adsorption on charcoal from water	Relative solubilities in solvent given in reference
Citric < adipic < caproic acids	Citric >>> adipic
Maleic < succinic < fumaric	Maleic > succinic > fumaric
Methylsuccinic < itaconic < citraconic	Methylsuccinic > itaconic << citraconic
Oxalic < acetic < glyoxylic	Oxalic << acetic and glyoxylic
Lactic = glyceric < pyruvic < propionic	All completely miscible at room temperature
Levulinic < valeric	Levulinic > valeric
Glycolic < acetic	—
Tartaric < malic < di = mono-bromosuccinic < succinic	Malic most soluble; tartaric and monobromosuccinic each nearly as soluble as the other; succinic least soluble

[a] Data from Linner and Gortner, *J. Phys. Chem.*, **39**, 35 (1935).

adsorption increased in the order acetic to valeric whether the temperature was 20, 40, 60, or 80 degrees. Acetic at 20° was adsorbed less than propionic at 60°. Adsorption decreased with increase in temperature.

F. EFFECT OF ADMIXTURE

Extensive studies of the effects of admixture have been made. Many of them were designed to test the Lundelius relation (see above). Angelescu and Comanescu[41] adsorbed picric acid on dried Merck *carbo medicinalis* from mixed solvents at initial concentrations of from 2 to 8%. The Lundelius relation held quite well for adsorption from the following mixtures, tested at concentrations of 1:3, 1:1, and 3:1 ethanol–chloroform; benzene–ether; ethanol–ether; acetone–benzene; ethanol–benzene; acetone–chloroform; also acetone–water 1:1; acetone–ethanol 1:1 and 1:3. The relation did not hold for acetone–ethanol 3:1 and acetone–water 3:1 and 1:3. To the ability of benzene to form a complex with picric acid[42] was ascribed the less than fair agreement in solutions of benzene with acetone or ethanol. Hydrogen bonding of solute with solvent and between the components of some of the mixed solvents probably also played a role.

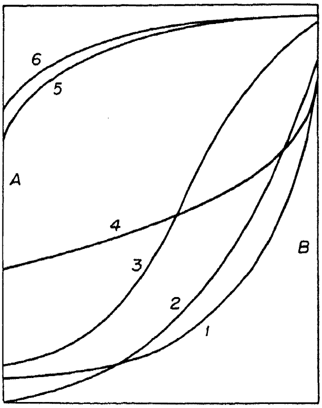

Fig. III-4. Adsorption of acids from water–alcohol mixtures. (A = 100% alcohol, B = 100% water.) The mixture was initially $^1/_{40}$ N with respect to the acid.[43] Adsorption (on 2 g. charcoal from 25 cc. solution) is plotted on the ordinate; the composition of the solvent is plotted on the abscissa. (*1*) acetic acid, (*2*) tartaric acid, (*3*) succinic acid, (*4*) oxalic acid, (*5*) benzoic acid, (*6*) salicylic acid.

Schilow and Pewsner[43] studied the adsorptions of acids (each at the one initial concentration of 1/40 N) from alcohol–water, alcohol–ether, alcohol–toluene onto purified charcoal. The isotherms were quite diverse for the alcohol–water system (Fig. III-4); less so for alcohol–ether, where the order of adsorbability was succinic < oxalic < benzoic < salicylic acid. In the alcohol–toluene system benzoic acid, though strongly adsorbed from either pure solvent was practically not adsorbed from the mixtures. The lack of clear correlations supported the authors' emphasis on the importance of competitive effects of solvents and solutes for the surface.

Results of these kinds are typical of the data in the literature. In some cases clear inverse relationships are found between solubility and extent of adsorption[44]; in other cases, anomalies of one kind and another appear.[45]

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[41] Angelescu and Comanescu, *Kolloid-Z.*, 44, 288 (1928); 50, 114 (1930).

[42] Fritzsche, *Ann.*, 109, 247 (1859).

[43] Schilow and Pewsner, *Z. physik. Chem.*, 118, 361 (1925).

Landt and Knop[46] found that the adsorption of fatty acids (acetic through valeric) on ash-free charcoal from water was always greater than from 0.02 *N* HCl solution. The difference was less for valeric than for acetic. The charcoal was of a type that adsorbs acids, and probably a competition was involved here. Phelps and Peters[47] obtained results more in agreement with the usual observation. They reported that the adsorption of organic acids on a charcoal increased with the acidity of the solution. It would be expected that the solubility of a fatty acid would be decreased by the presence of HCl, since its ionization would be suppressed. However, it is not an invariable observation that well ionized substances are poorly adsorbed. The work with anionic and cationic surface active agents shows that these substances are adsorbed at liquid–vapor and liquid–solid interfaces.[48]

Angelescu and Comanescu[49] reported that the adsorption of an organic acid is decreased in the presence of its salt. The presence of the salt of the acid is known to cause an increased miscibility of the free acid with water,[50] while the presence of an unrelated inorganic salt has the reverse effect. Salting into and out of solution has been mentioned above. It may be added here that Fromageot and Wurmser[51] found that salts of the organic acids formic, acetic, propionic, succinic, citric, and pyruvic were adsorbed less strongly than the corresponding free acids from 0.01 *N* aqueous solution by purified charcoal.

G. COMPARISON OF SOLVENTS

The effects of solubility on extent of adsorption may be examined by comparing adsorption from different solvents, whether homologous solvents or solvents of different chemical types. Wöhler and Wenzel[52] measured the adsorption of a high-molecular (nonvolatile, liquid) paraffin from pentane, 103° boiling point ligroin, and 147° ligroin at —14°, 14°, and room temperature on Merck's *carbo animalis* activated at 500° in nitrogen. The data are shown in Figure III-5. Adsorption from pentane was quite marked, falling off to 103° ligroin and to 147° ligroin, that is, in the reverse order of the probable solubilities. The authors speak of this as a sort of reversal of Traube's rule: The strength of adsorption of a substance from solvents which form an homologous series falls with rise in carbon content of the solvent. The temperature dependence of the adsorption was small. It was observed that the surface tension of pure pentane was not changed by the presence of 1.2% paraffin, though adsorption (on charcoal) was so marked.

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[44] Sata, *Kolloid-Z.*, 49, 275 (1929). Heymann and Boye, *Z. physik. Chem.*, A150, 219 (1930). Herz and Levi, *Kolloid-Z.*, 50, 21 (1930). Landt and Knop, *Z. Elektrochem.*, 37, 645 (1931).

[45] Sata and Kurano, *Kolloid-Z.*, 65, 283 (1933).

[46] Landt and Knop, *Z. physik. Chem.*, A162, 331 (1932).

[47] Phelps and Peters, *Proc. Roy. Soc. London*, A124, 554 (1929).

[48] A. M. Schwartz and J. W. Perry, *Surface Active Agents*. Interscience, New York, 1949.

[49] Angelescu and Comanescu, *Chem. Abstracts*, 23, 2866 (1929).

[50] Bury and Mends, *J. Chem. Soc.*, 1939, 742.

[51] Fromageot and Wurmser, *Compt. rend.*, 179, 972 (1924).

[52] Wöhler and Wenzel, *Kolloid-Z.*, 53, 273 (1930).

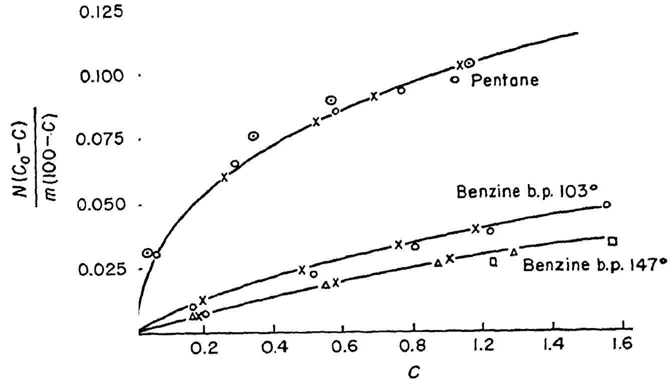

Fig. III-5. Adsorption of paraffin onto *carbo animalis* from different solvents at various temperatures.[52] N = weight of solvent in grams; m = weight of adsorbent in grams; C_0 = initial concentration in weight percent; C = final concentration in weight percent.

×	in pentane	at	−14.5°	
○	” ”	”	+14.5°	
×	” benzine (b.p. 103°)	”	−19.5°	
○	” ” ” ”	”	+16.7°	
□	” ” ” ”	”	+70.0°	
×	” ” ” 147°	”	+17.5°	
△	” ” ” ”	”	+17.0°	+3% ether
⊙	” ether	”	−18°	

When chemically similar solvents were compared by Cassidy[53] it was observed that adsorption on charcoal from ligroin was less than that from petroleum ether for the acids lauric, palmitic, and stearic. The order of adsorption lauric < palmitic < stearic was the same in the two solvents, but was displaced toward lower adsorption in ligroin, in which the acids are more soluble.

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[53] Cassidy, *J. Am. Chem. Soc.*, 62, 3073 (1940).

A substance may be adsorbed on a given solid from solvents of different chemical types. In such cases a comparison of relative adsorbability and relative solubility is interesting. Patrick and D. C. Jones[54] found that acetic acid was adsorbed on silica gel in increasing amounts at a given equilibrium concentration from the solvents nitrobenzene, toluene, carbon tetrachloride, carbon disulfide, and kerosene. Other solutes were also examined. These authors concluded that, in general, adsorption of a solute such as acetic acid, formic acid, benzoic acid, and nitrobenzene upon silica gel was greater the lower its solubility in the solvent. They suggested, to account for some of their observations, that the solute perferentially wets the gel and concentrates in its pores, its solubility while filling the pores being lowered due to the highly concave surfaces presented to the solvent. This idea was based on the theories of Patrick and McGavack.[55]

TABLE III-6

Comparison of Extents of Adsorption with Solubilities of Isomeric Hydroxybenzoic Acids (*ortho*, *meta*, and *para*) from Different Solvents[57]

Solvent	Order of adsorption	Order of solubility
Methyl alcohol	$m < p < o$	$o > p > m$
Ethyl alcohol	$m < p < o$	$o > p > m$
Propyl alcohol	$m < p < o$	$o > p > m$
Ethyl ether	$o < m < p$	$o >> p > m$
Acetone	$m < o < p$	$o > m > p$

Note: Adsorption was measured from solutions of initial concentration 0.01 M. The adsorbent was Merck *carbo medicinalis*, and 1 g. was used in each case.

The order of adsorption of benzoic acid on a dried phenol-formaldehyde resin from different solvents was found to be methanol < benzene < ethanol < acetone << carbon tetrachloride < carbon disulfide << water. The order of solubility is methanol > ethanol > acetone >> benzene > carbon bisulfide > carbon tetrachloride >> water.[56] The comparison of isomeric hydroxybenzoic acids is shown in Table III-6.[57]

Yermolenko and Levina[58] extended the observations of Heymann and Boye, and others, reported above by studying the *simultaneous adsorption of two acids* (each originally 0.005 N) in mixed solvents, on Kahlbaum animal charcoal. The solvents were chosen to be both "nonpolar" (CCl_4–C_6H_6): one nonpolar, the other polar but not affecting the polarity of the first (CCl_4 – toluene, C_6H_6 – toluene, C_6H_6 – $CHCl_3$); one nonpolar, the other polar and capable of affecting the polarity of the first (C_6H_6 – ethanol, CCl_4 – ethanol, CCl_4 – acetone); and both polar (water–ethanol, acetone–ethanol, chloroform–acetone, chloroform–ethanol). The behaviors were quite complex. The authors found a regular dependence of the adsorption on the polar properties of the medium, but they would seem to agree with others that a general inverse relation between extent of adsorption and solubility is far from being satisfied. They observed that the character of the isotherm of either of the acids was not fundamentally changed by the presence of the other acid in the mixed medium.

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[54] Patrick and D. C. Jones, *J. Phys. Chem.*, 29, 1 (1925).

[55] McGavack and Patrick, *J. Am. Chem. Soc.*, 42, 946 (1920).

[56] Bhatnagar, Kapur, and Puri, *J. Indian Chem. Soc.*, 13, 679 (1936).

[57] Sata and Watanabe, *Kolloid-Z.*, 70, 159 (1935).

[58] Yermolenko and Levina, *Acta Physicochim. U. R. S. S.*, 10, 451 (1939).

Some investigators have concluded rather definitely that for a given adsorbent such as silica gel the relative adsorptions of solutes are ordered oppositely to their solubilities.[59] Others have found no correlations.[60] Sata and Kurano[61] postulated that adsorbability and solubility in general proceed antibatically, and that when this is observed not to be the case then some secondary cause disturbs the behavior.

Bartell and Fu[62] discussed the role of solubility in adsorption and concluded that the influence of solubility upon extent of adsorption can be determined legitimately only if the solvents being used have the same interfacial tension against the adsorbent in question. Thus, benzene and carbon tetrachloride show approximately the same adhesion tension against silica, indicating that the interfacial tensions must be of comparable magnitude. One would then be justified in comparing the results obtained with these two liquids. From such comparisons the authors conclude that, in general, if the solvents being compared show the same interfacial tension against the adsorbent then adsorption will occur to a greater extent from those solvents in which the adsorptive is less soluble. This conclusion would seem to be of the kind most likely to be widely valid.

From the evidence presented in the first part of this section it seems that concentration of adsorptive is related to adsorption in a complicated way. That is to say, apart from the expected behavior as shown in the ordinary isotherms for dilute solutions, it is apparent that from a given solvent a solute can be positively adsorbed (from dilute solution) or negatively adsorbed (from concentrated solution).

This may throw light on the effects of solubility upon adsorbability, as has been suggested elsewhere, or it may be a matter of inhomogeneity of the surfaces, or it may be due to some other factors. It would certainly seem, however, from the sampling of evidence presented so far in this chapter that, despite certain attractive justifications for the hope, no really broad and general relation can be found between relative solubility and relative adsorbability.

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[59] Patrick and D. C. Jones, *J. Phys. Chem.*, 29, 1 (1925).

[60] Roychoudhury, *Kolloid-Z.*, 57, 308 (1931).

[61] Sata and Kurano, *Kolloid-Z.*, 65, 283 (1933).

[62] Bartell and Fu, *J. Phys. Chem.*, 33, 678 (1929).

III. SURFACE TENSION OF THE SOLVENT

Syrkin and Poliakow[63] studied the adsorption of tetraethylammonium iodide on a purified wood charcoal from a number of solvents. They found that, in general, adsorption was greater from solvents with higher surface tensions and higher dielectric constants. The observed order of adsorption was from ethanol < from methanol < from water. A relation between higher surface tension of the pure solvent and higher adsorbability from that solvent was shown in the observed order of adsorption (the figures in parentheses are the surface tensions): from ethanol (22) < from acetone (23) < from methanol (23) < from anisaldehyde < from benzaldehyde (39.2) < from water (74). No certain correlation was observed with other characteristic constants of the solvents, such as dipole moment.

IV. POLARITY OF THE SOLVENT

It will be shown in the next chapter that polarity of adsorptive is not always related to extent of adsorption; hence it is to be expected that no general relation can be found between extent of adsorption and polarity of the solvent, except in special cases where the solvent plays an exaggerated role in the adsorption. These latter cases may be found for adsorption at the solution–air interfaces. The role of polarity of the solvent in adsorption has been investigated by seeking correlations between relative extent of adsorption and (*a*) relative dipole moments of solvents, (*b*) relative polarizability of solvents, and (*c*) relative dielectric constants of the solvents that are compared. The *polarity of the solvent* may influence the extent of adsorption at saturation of the surface through its effect on the orientation of the adsorptive molecules in the interface. This latter influence has been studied by Taubman for the surfaces of solutions in polar and less polar solvents and is described in Chapter I. The polarity of the solvent may also affect the extent of adsorption as it works toward making the adsorptive more or less soluble.

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[63] Syrkin and Poliakow, *Kolloid-Z.*, 55, 33 (1931).

Heymann and Boye[64] made an extensive study of adsorption onto ash-free charcoal in relation to the *dielectric properties* of the solvent. They pointed out in their discussion that theories of adsorption from solution must take into account the adsorption of solvent. If adsorbability depends upon the dipole moment of the adsorptive (the permanent dipole of the adsorptive polarizing the adsorbent and interacting attractively with it, as is thought to occur in some gas–solids adsorptions) then it would follow that a given substance would be less well adsorbed from a solvent with a high dipole moment than from one with a low moment, since the former would compete more effectively for the surface than the latter (the moment of the solute being assumed to be little affected by that of the solvent). However, it cannot be expected that the dipole moment as derived from measurements in the gaseous or dilute solution phases can apply to the dense solution state. Polarizability effects, permanent moments, and orientation effects in the solvent need to be considered, as do the effects of solvent on the solute. Solutes with moments higher than the solvent often associate in solution, whereupon the dipole moment of the solute in solution is greatly affected. On top of these considerations is the added uncertainty that little is known about the mutual influence of solvent and solute in the interface. It is therefore evident that, even in favorable cases, very complicated behaviors are being dealt with, so that the most that can be expected are qualitative relations between the adsorption of a solute and the polar nature of the solvent. The authors point to the work of Wo. Ostwald[65] on the connection between the stability of sols and the dielectric structure of the solvent, and of Sakurada[66] on the extent of swelling of gels and the molecular polarization of solvent mixtures (in both of which processes adsorption of the solvent plays a role) as offering evidence for the influence of the polarity of the solvent on adsorption. Their own work with single and mixed solvents showed, on the whole, a certain correlation between increasing adsorption and decreasing *dipole moment* or decreasing molar polarization of the solvent; however, there were many exceptions. This also seems to be the conclusion of other workers.[67]

Jacques and Mathieu[68] measured the adsorption of benzophenone and other substance onto alumina from a variety of solvents and from mixtures of solvents. They enunciated, on the basis of their experiments, the follow-

[64] Heymann and Boye, *Z. physik. Chem.*, **A150**, 219 (1930).

[65] Wo. Ostwald, *Kolloid-Z.*, **45**, 114, 331 (1928).

[66] Sakurada, *Kolloid-Z.*, **48**, 277, 353 (1929); **49**, 52, 178 (1929).

[67] Sata and Kurano, *Kolloid-Z.*, **60**, 137 (1932). Ginzburg, *Chem. Abstracts*, **37**, 2243 (1943).

[68] Jacques and Mathieu, *Compt. rend.*, **221**, 293 (1945).

ing rules: (*1*) in a binary mixture the component with the higher *dielectric constant* is better adsorbed; (*2*) in binary mixtures of a given component with other substances the extent of adsorption of the component with the higher dielectric constant increases as the difference in the dielectric constants of the two; and (*3*) in ternary mixtures it is still the constituent with the highest dielectric constant which is most adsorbed. There was, however, no clear relation found between the extent of the adsorption and the dipole moment, or the polarizability. The data given by these authors are collected into Table III-7. Syrkin and Poliakow[69] found no relation between extent of adsorption of tetraethylammonium iodide on charcoal and the dipole moment of the solvent. The adsorption took the order: from ethanol < from methanol < from water. This order suggested to the authors that adsorption decreased with dielectric constant of the solvent and decreased with increase in molecular refraction of the solvent. Adsorption was found to be negligible from propionitrile and from nitrobenzene "in spite of their high dipole moments."

TABLE III-7

Relation between Extent of Adsorption onto Alumina and Magnitude of the Dielectric Constant[a]

Solvent	Hexane	Benzene	Ethyl ether	Chloroform	Dichloroethane	2-Butanol	Acetone	Ethyl alcohol	Methyl alcohol
Dielectric constant (ϵ)........	1.88	2.29	4.37	5.2	10.4	15.5	21.5	26	31.2
Dipole moment ($\lambda \times 10^{18}$).......	0	0	1.13	0.99	1.27	1.65	2.90	1.70	1.67
Polarizability $\alpha \times 10^{24}$...	12	10	8.8	8.3	9.6	—	6.3	—	3.2

Orders of Adsorption (Benzophenone, $\epsilon = 13.3$)

hexane < chloroform
dichloroethane < 2-butanol
benzene < acetone
chloroform < methyl alcohol
benzene < chloroform
benzene < ethyl alcohol

benzene, chloroform, or dichloroethane < benzophenone < 2-butanol or acetone

[a] Data from Jacques and Mathieu.[68] No quantitative data on adsorptions given.

The data of Angelescu and Comanescu[70] for the adsorption of picric acid onto charcoal from alcohol–benzene mixtures shows that the curve for adsorption *vs.* percent alcohol goes through a minimum which extends from near 25 to 75% alcohol (mole percent). Ostwald[71] pointed out that in this solvent mixture a maximum in the dipolar properties appears at 35 mole percent alcohol, indicating a condition in the mixture which would aid solution of the picric acid by stabilizing and isolating the ions. A maximum of solubility for picric acid also occurs in the solvent mixture, though displaced toward a higher alcohol content. The curve for adsorption of picric acid goes through a minimum. This is interpreted to show how an increase in dipolar nature, with its influence on increased solubility, may work against adsorption. Complicated relations were found for mixtures of alcohol with acetone, with chloroform, and with ether.

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[69] Syrkin and Poliakow, *Kolloid-Z.*, 55, 33 (1931).

[70] Angelescu and Comanescu, *Kolloid-Z.*, 44, 288 (1928).

[71] Wo. Ostwald, *Kolloid-Z.*, 45, 331 (1928).

V. POLARITY OF THE ADSORBENT

The polarity of an adsorbent can be related, in many instances, to the extent of an adsorption, or especially to the direction of increasing adsorption in an homologous series of compounds. Bartell and Scheffler[72] compared the adsorptions over the entire concentration range of lower aliphatic alcohols from benzene onto silica gel and onto purified charcoal (Figs. III-6 and III-7). It was observed that the alcohols were adsorbed preferentially on the silica gel, the order of adsorption being isoamyl $<$ n-butyl $<$ n-propyl $<$ ethyl $<$ methyl. On charcoal, the benzene was adsorbed preferentially, but the order of adsorption of the alcohols was the same. This agrees with the general observation that silica gel and charcoal are opposite in polarity. Bartell and Osterhof,[73] using a pressure of displacement method and the adhesion tension values for water against ether-extracted lampblack (54.74) and against silica ("Tripoli") (81.5) and α-bromonaphthalene against silica (41.92 dynes/cm.), found the order of adhesion tension of "average C.P. grade" liquids against the carbon black almost exactly the reverse of that against silica. The order of decreasing adhesion tension against lampblack was almost the same as that of the decreasing interfacial tension against water. The data are given in Table III-8. The data obtained are of comparative value. The actual magnitudes depend upon the pretreatment of the surface.

Bartell and Almy[74] found that the relative heats of wetting of a given silica gel by a series of liquids are the same as given by the series with another sample of gel for the same surface area wetted. For example, the heat of wetting with benzene is, for all gels examined, 0.66 times that with water. These authors chose benzene as a standard reference liquid, and, utilizing the constant ratios found, set up a table of the relative heats of wetting of nine liquids, adsorbed on a number of gels (Table III-9). According to these investigators it is possible to calculate the heat of wetting of a silica gel by any of the liquids if the heat of wetting by one of the liquids is known.

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[72] Bartell and Scheffler, *J. Am. Chem. Soc.*, 53, 2507 (1931).

[73] Bartell and Osterhof, *J. Phys. Chem.*, 37, 543 (1933); *Ind. Eng. Chem.*, 19, 1277 (1927).

[74] Bartell and Almy, *J. Phys. Chem.*, 36, 985 (1932).

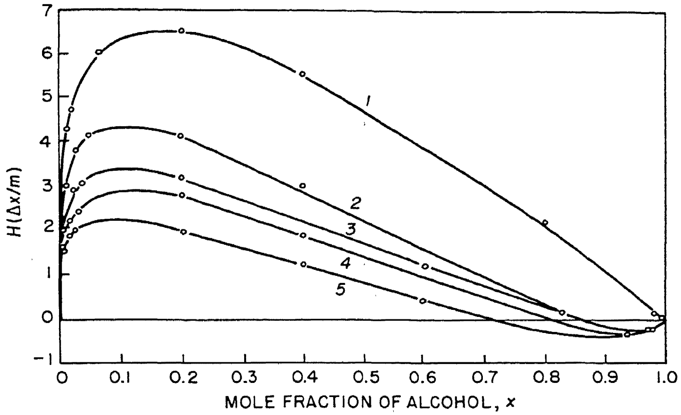

Fig. III-6. Adsorption of the alcohol by silica from binary mixtures of various alcohols with benzene over the entire concentration range.[72] H = total number of millimoles in solution; Δx = mole fraction change due to adsorption; m = weight of adsorbent in grams. (*1*) methyl alcohol, (*2*) ethyl alcohol, (*3*) *n*-propyl alcohol, (*4*) *n*-butyl alcohol, (*5*) isoamyl alcohol.

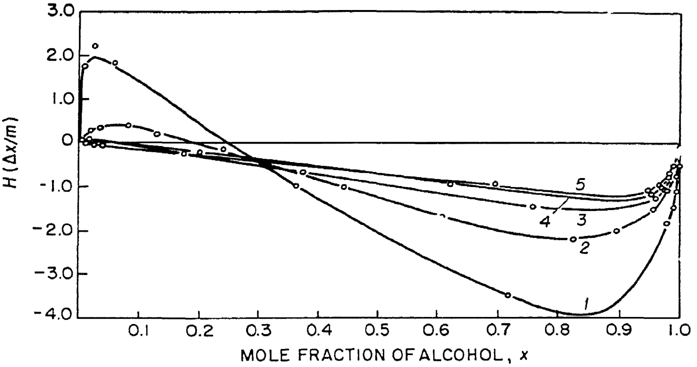

Fig. III-7. Adsorption of the alcohol by purified ash-free blood charcoal from binary mixtures of various alcohols with benzene over the entire concentration range.[72] See Figure III-6 for explanation of symbols.

Bartell and Lloyd[75] showed that by changing the conditions of activation of purified charcoal it was possible to alter the behavior of the charcoal.

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[75] Bartell and Lloyd, *J. Am. Chem. Soc.*, 60, 2120 (1938).

TABLE III-8

Adhesion and Interfacial Tension Data[73]

Liquid	Adhesion tension against Extracted lampblack	Adhesion tension against Silica	Interfacial tension against water
Carbon disulfide	90.77	43.2	48.1
Carbon tetrachloride	86.38	39.5	44.5
α-Bromonaphthalene	88.81	41.1	41.6
Toluene	82.10	53.4	36.1
Benzene	81.03	51.2	34.6
Chloroform	79.83	58.7	31.6
Decalin	76.38	—	26.7
Nitrobenzene	79.58	61.4	25.3
Tetralin	76.70	—	22.4
Butyl acetate	65.78	72.1	13.2
Ethyl carbonate	65.55	—	12.4
Amyl acetate	63.68	73.7	10.9
Ether	59.85	—	10.7
Propyl acetate	63.09	74.4	9.6
Ethyl acetate	59.07	76.1	6.8
Aniline	60.22	73.8	5.7
Amyl alcohol	58.77	77.5	5.0
Benzyl alcohol	58.73	—	4.8
Isobutyl alcohol	56.60	80.7	1.8

TABLE III-9

Heats of Wetting of Silica by Certain Liquids Relative to Benzene[74]

Liquid	Heat of wetting, $-Q$	Liquid	Heat of wetting, $-Q$
Acetone	1.64	Ethylbenzene	0.85
Water	1.51	Chloroform	0.82
Nitrobenzene	1.21	Carbon tetrachloride	0.69
Benzene	1.00	Hexane	0.56
Chlorobenzene	0.94		

Organophilic charcoals could be prepared (by high-temperature activation) which preferentially adsorbed benzene from benzene–ethanol solutions. The same charcoal activated at a low temperature in a highly oxidizing atmosphere became hydrophilic, and behaved like silica gel in adsorbing alcohol preferentially from benzene solution. Intermediate behaviors could also be produced (Table III-3).

It is evident from the foregoing data and discussion that both the solvent and the adsorbent phases can play an important role in an adsorption process. The observation of Bartell and Almy[74] that the relative order of heats of wetting of a variety of liquids is the same for all samples of silica gel investigated, taken with Bartell and Osterhof's[73] conclusion that the order of increasing adhesion tension of liquids against silica is the reverse of that against charcoal, suggests a basis for choosing adsorbent, developer, and eluent in chromatographic analyses. These latter investigators also pointed out that, other factors being equal, that liquid which gives the higher interfacial tension against a solid will be displaced by the other liquid.

CHAPTER IV

Relations between Relative Extent of Adsorption and Properties of Adsorptive

I. INTRODUCTION

At the molecular level the factors which may influence extent of adsorption are so numerous, arising not only from the molecules of the adsorptive but from the solvent and adsorbent molecules as well, that a correlation, which in a chosen case can appear very reliable, can always be shown to be inapplicable in other cases. Correlations will appear when in some given system the molecular property in question plays so outspoken a role in influencing the adsorption that other factors become of negligible consequence beside it. These relations are contingent in nature; they may be invalidated by circumstances that arise when the system is changed.

When adsorption at mobile interfaces is being considered, the extent of adsorption is usually measured through the lowering of interfacial tension. At immobile interfaces it is usually measured by the extent to which the substance disappears from the gas or liquid phase when solid is introduced. As usual, adsorption from solution to a solid will be given most space. It is not pretended that this chapter represents a complete report of the literature. Such a report would require many times the space allotted. An attempt has been made, however, to cover as many types of correlation as possible, and to give leading references to the literature.

II. ADSORPTION AND CHEMICAL STRUCTURE

If the concept of homology is to have a useful application it must be through the chemical similarity and regular change in physical properties which it implies. Relative adsorption in an homologous series, insofar as it is dependent only on the functional group, should change little over the series; insofar as it is dependent on the physical properties it should change in a regular fashion along the series. An examination of the relative adsorption of homologs should therefore give considerable evidence of value in setting up correlations and predicting adsorbability.

For the effects of chemical groups the adsorptions of corresponding compounds should be examined. Perhaps then a series could be set up, relating the relative "adsorbabilities" of functional groups. A correlation such as this would undoubtedly be contingent on many factors; however, it might nonetheless be of considerable value, a contingent correlation being better than none.

The material in this section is classified according to chemical functional group, and further into adsorptions at mobile and immobile interfaces. The reason for this classification is that the phenomena at mobile interfaces are relatively easily reproducible, for which reason the work of different laboratories is expected to show agreement. On the other hand, immobile interfaces are often difficult to reproduce, even in the same laboratory at different times, and so agreement between the data of different laboratories is not to be expected unless the phenomena being compared depend not upon the variable interface but upon some factor which is not variable.

1. Hydrocarbons and Some Derivatives

Micheli[1] found the order of effectiveness in lowering the surface tension of water, when hydrocarbons were adsorbed from the vapor phase in air onto drops, to be pentane < hexane < heptane < benzene at 25 and 30°. The order for the surface tension lowering of mercury was pentane < hexane < benzene < heptane < octane. Cassel and Formstecher[2] found, using a maximum bubble pressure method, the order butane < hexane < heptane against water. Pearce and Goergen[3] adsorbed hydrocarbons on stannous oxide. The order of adsorption at 0° was ethylene < acetylene < ethane; at 78.5° ethylene < ethane < acetylene; and at 100° ethylene < ethane.

In studies of adsorption from solution, Baum and Broda[4] dissolved paraffin in benzene (0.300 g. per 100 cc.) and treated the solution with 5 g. pulverized charcoal. The order of adsorption, in terms of melting range of the paraffin, was 42–44° < 46–48° < 56–58° < 68–72°. Extent of adsorption thus increased with average "chain length." The heats of adsorption were stated to be inconsiderable.

Adsorption of the pure substances can be measured in terms of adhesion tension. Data from Bartell and Osterhof[5] are given in Chapter III, Table 8. For the order of adsorption of hydrocarbons from mixtures on to silica gel, Mair and Forziati[6] found *n*-heptane $<$ toluene; and 2,2,4-trimethylpentane $<$ "diisobutylene" $<$ toluene. Their experience[7] was summed up in the statement that for components of approximately equal molecular weights, and with certain limitations on the type and configuration of the aromatic rings, the order of increasing adsorption on silica is paraffins, naphthenes, monoolefins, diolefins, 1-, 2-, 3-, and 4-ring aromatic hydrocarbons. Confirmatory of this was the order of adsorption from mixtures on columns of silica gel reported by Mair.[8]

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[1] Micheli, *Phil. Mag.* (7), 3, 895 (1927).

[2] Cassel and Formstecher, *Kolloid-Z.*, 61, 18 (1932).

[3] Pearce and Goergen, *J. Phys. Chem.*, 32, 1423 (1928).

[4] Baum and Broda, *Trans. Faraday Soc.*, 34, 797 (1938).

[5] Bartell and Osterhof, *Ind. Eng. Chem.*, 19, 1277 (1927).

It is interesting to recall in connection with predictions of adsorbability along an homologous series the statement of Rossini,[9] in summarizing data on heats of combustion of *n*-paraffin hydrocarbons and *n*-primary alcohols, that the introduction of a CH_2 group does not produce a constant increment in this property until the number of carbon atoms exceeds five. This is interpreted as indicating that an atom in a chain extends its influence as far as the atom second removed from it. Only in chains with five or more carbon atoms will the extension of the chain consist in introducing additional CH_2 groups in the middle of the molecule under effectively constant conditions.[10]

2. Alcohols and Phenols

Adsorption at the air–solution interface may be measured in terms of surface tension lowering. For the aqueous solution–air interface Duclaux[11] found the order of increasing surface activity to be methyl, ethyl, and amyl alcohols. This order was confirmed by Traube[12] and extended by King,[13] who reported the order butyl $<$ isoamyl $<$ octyl alcohol, as determined by a drop-weight method. A more detailed study made by Weber and Sternglanz[14] on homologous and isomeric alcohols has been reported (Table III-2).

Bartell and Davis[15] observed the order of effectiveness of alcohols in lowering the boundary tension at the interfaces water–air, water–*n*-hep-

[6] Mair and Forziati, *J. Research Natl. Bur. Standards,* 32, 151 (1944).

[7] Mair and Forziati, *J. Research Natl. Bur. Standards,* 32, 165 (1944).

[8] Mair, *J. Research Natl. Bur. Standards,* 34, 435 (1945).

[9] Rossini, *J. Research Natl. Bur. Standards,* 13, 21, 189 (1934).

[10] For a discussion of additivity of bond energies, see Sturtevant, "Calorimetry," in Weissberger, ed., *Physical Methods of Organic Chemistry.* 2nd ed., Interscience, New York, 1949, Part I, p. 731 ff.

[11] Duclaux, *Ann. chim. phys.* (5), 13, 76 (1878).

[12] Traube, *Ann.,* 265, 27 (1891).

[13] King, Kansas Agr. Expt. Sta., *Tech. Bull.* 9 (1922).

[14] Weber and Sternglanz, *Z. physik. Chem.,* A169, 241 (1934).

[15] Bartell and Davis, *J. Phys. Chem.,* 45, 1321 (1941).

tane, water–benzene, and water–methyl *n*-amyl ketone to be ethyl $<$ *n*-propyl $<$ *n*-butyl alcohol.

Trappe[16] set up an elution series of substances for use in chromatography (see Table IV-8). The eluting efficiency of these substances is undoubtedly due in part to their adsorbability, the more strongly adsorbed ones being able to elute adsorbed substances more effectively. On the basis of data from various sources it appeared that polar substances adsorbed the alcohols in the order 1-propanol $<$ ethanol $<$ methanol $<$ water.

Boyd and Harkins[17] found the heats of immersion shown in Table IV-1. In studies of adsorption onto silica gel from the gaseous phase Gyani and Ganguly[18] found the order of extent of adsorption to be, at high relative pressures, butanol $<$ propanol $<$ ethanol $<$ methanol; and at low relative pressures propanol $<$ ethanol $<$ butanol $<$ methanol. The relative pressure was the ratio of the observed pressure to the saturation pressure at 35°. When the adsorptions were plotted against observed pressure, the order was methanol $<$ ethanol $<$ propanol $<$ butanol.

Adsorption of alcohols from solution to solid adsorbents was studied by Bartell and Scheffler.[19] Order of adsorption from benzene onto silica at low concentrations was isoamyl $<$ *n*-butyl $<$ *n*-propyl $<$ ethyl $<$ methyl alcohol (Fig. III-6). From benzene onto ash-free blood charcoal the same order was found (Fig. III-7). The adsorptions on silica were, for a given alcohol, greater than on charcoal. Heymann and Boye[20] found a similar order of adsorption of alcohols from dilute solutions in carbon tetrachloride on dry ash-free wood charcoal. For adsorption at a given equilibrium concentration from water at 18° onto Merck animal charcoal, Amiot[21] found the order to be methyl $<$ ethyl $<$ isopropyl $<$ propyl $<$ isobutyl $<$ butyl $<$ isoamyl. A similar order for adsorption by quartz from aqueous solutions was found by Pospelova.[22]

TABLE IV-1

Heats of Immersion[17] (Calories per gram of adsorbent at 25°C.)

Pure adsorptive	Adsorbent				
	TiO_2	SiO_2	SnO_2	$BaSO_4$	Graphite
Butyl alcohol	0.829	0.235	0.255	0.375	—
Ethyl alcohol	1.20	0.291	—	—	1.69
Water	1.24	0.334	0.345	0.517	1.79

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[16] Trappe, *Biochem. Z.*, 305, 150 (1940).

[17] Boyd and Harkins, *J. Am. Chem. Soc.*, 64, 1190 (1942).

[18] Gyani and Ganguly, *J. Phys. Chem.*, 49, 226 (1945).

[19] Bartell and Scheffler, *J. Am. Chem. Soc.*, 53, 2507 (1931).

[20] Heymann and Boye, *Kolloid-Z.*, 63, 154 (1933).

[21] Amiot, *Compt. rend.*, 202, 1852 (1936); 208, 1575 (1939).

[22] Pospelova, *J. Phys. Chem. U. R. S. S.*, 11, 99 (1938).

The order of adsorption of nitrophenols onto calcium carbonate from benzene was found, in a chromatographic method, to be *o*- $<$ *m*- $<$ *p*-.[23] Amiot,[24] giving no experimental details, found the adsorption on charcoal from water to be the same for phenol, 2,2-dihydroxy-, 1,3-dihydroxy-, and 1,3,5-trihydroxybenzenes.

3. Carbonyl Compounds

The Traube rule was found by Flumiani and Corubolo[25] to hold for the aldehydes acetaldehyde, propionaldehyde, *n*-butyraldehyde, and isobutyraldehyde, this being the order of increasing adsorption from water solution onto animal charcoal. Formaldehyde was an exception, the course of its isotherm being different from that of the others. In adsorption from methyl alcohol,[26] the normal order of increasing adsorption from formaldehyde to butyraldehyde was followed. In ethyl alcohol, acetaldehyde was less well adsorbed than formaldehyde; in propyl alcohol, propionaldehyde was less well adsorbed than acetaldehyde, indicating that when the aldehyde is dissolved in an alcohol with the same number of carbon atoms it is less well adsorbed. Solubilization, such as this may be, has been mentioned elsewhere (Chapter III). In examining the effect of solvent, Flumiani and Ruzdic[27] compared the adsorption of aldehydes from the saturated vapor with that from solution, and with the adsorption of pure solvent from the vapor. Animal charcoal had a higher capacity for water than for aldehydes from the vapor, yet adsorption of aldehydes from solution was greater than from the vapor. This made it appear to the investigators that for the most part the solvent was not concerned in the adsorption. However, adsorption from alcoholic solution was far lower than from the saturated aldehyde vapor, though from the pure vapor phases aldehydes and alcohols were adsorbed to almost the same extent. It might be that these results could be explained on the basis of hydrate and acetal formation, which is known to be almost instantaneous, and that it is these forms which are adsorbed. Comparison with the saturated vapor would then not be legitimate.

Sata[28] found the adsorption from water to Merck animal charcoal to be in the order cyclohexandione $<$ hydroquinone $<$ quinone. Miculicich[29] found the adsorption of aldehydes on a medicinal charcoal from 0.005, 0.0150, or 0.0450 M aqueous hydrochloric acid solutions to be formaldehyde $<$ acetaldehyde $<$ propionaldehyde $<$ isobutyraldehyde $<$ butyraldehyde as judged by the equilibrium concentrations necessary to produce an adsorption of 2.25 milimoles per gram of charcoal. Using a chromatographic technique, Zechmeister, McNeely, and Sólyom[30] observed the order of adsorption from 2:1 chloroform:benzene on Neutrol Filtrol to be *cis*- $<$ *trans*-benzoin oxime; and *cis*- $<$ *trans*-anisoin oxime.

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[23] Karrer and Nielsen, *Festschrift Zangger*, 2, 954 (1935).

[24] Amiot, *Compt. rend.*, 208, 1575 (1939).

[25] Flumiani and Corubolo, *Rad. jugoslav. Akad.*, 241, 251 (1931); *Chem. Abstracts*, 33, 7170 (1939).

[26] Flumiani and Engelsrath, *Rad. jugoslav. Akad.*, 249, 15 (1938); *Chem. Abstracts*, 33, 7171 (1939).

[27] Flumiani and Ruzdic, *Rad. jugoslav. Akad.*, 261, 23 (1938); *Chem. Abstracts*, 34, 7691 (1940).

[28] Sata, *Kolloid-Z.*, 49, 275 (1929).

4. Fatty Acids

The aliphatic carboxylic acids have been much used in studies on adsorption because they are accessible, stable, readily purified, easily analyzed for, soluble enough in water to give a reasonably long series, and soluble in organic solvents, and because their other physical properties such as boiling and melting points do not raise serious experimental difficulties. It has been found that the surface activity of the fatty acids in aqueous solution increases with the number of CH_2 groups in the chain.[31] The regularity of this increase was observed by Traube[32] and has been repeatedly confirmed in its principle.[33] The quantitative relationships observed have been discussed in Chapter II. Qualitatively, all the experiments agree in showing that the extent of the adsorption at the surface of pure aqueous solutions of the normal fatty acids increases, for a given equilibrium concentration, in the order formic, acetic, . . ., decanoic (capric) (Fig. II-4). Analogous order holds when the isoacids, isobutyric and isovaleric, are compared at the same concentration.[32] When isomeric acids are compared it is found that isobutyric is somewhat better adsorbed than butyric at the same equilibrium concentration.[32]

Weigner, Magasanik, and Virtanen[34] observed the Traube order to hold in adsorption to the surface of aqueous solutions of acetic, propionic, and butyric acids. The adsorption was increased by the presence of 2 N sodium chloride, but the order was not changed.

The Traube rule was observed to hold for the adsorption of acetic, propionic, and butyric acids at the air–solution and paraffin–solution interfaces by Fowkes and Harkins.[35]

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[29] Miculicich, *Arch. exptl. Path. Pharmakol.*, 172, 373 (1933).

[30] Zechmeister, McNeely, and Sólyom, *J. Am. Chem. Soc.*, 64, 1922 (1942).

[31] Duclaux, *Ann. chim. phys.* (5), 13, 76 (1878).

[32] Traube, *Ann.*, 265, 27 (1891).

[33] Szyszkowski, *Z. physik. Chem.*, 64, 385 (1908). Weber and Sternglanz, *Z. physik. Chem.* A169, 241 (1934). King, Kansas Agr. Expt. Sta., *Tech. Bull.* 9, (1922). Merkel, *Kolloid Beihefte*, 45, 413 (1937). Ward, *Trans. Faraday Soc.*, 42, 399 (1946).

[34] Wiegner, Magasanik, and Virtanen, *Kolloid-Z.*, 28, 51 (1921).

The results of experiments in which fatty acids are adsorbed at immobile interfaces fall into three classes when the extents of adsorption at equal equilibrium concentrations are compared for different acids:

Class a. Traube's order applies.
Class b. An order the reverse of that given by Traube applies.
Class c. All the fatty acids are adsorbed to approximately the same extent.

The existence of these three types of results emphasizes the influences of the phases on the adsorption. The influence of the properties of the molecule needs some comment.

Class a. Freundlich[36] found the order of increasing adsorption of normal fatty acids from aqueous solution and from other solutions onto a blood charcoal to be formic, acetic, propionic, butyric. The same order for acetic through valeric acids from water onto animal charcoal was re-

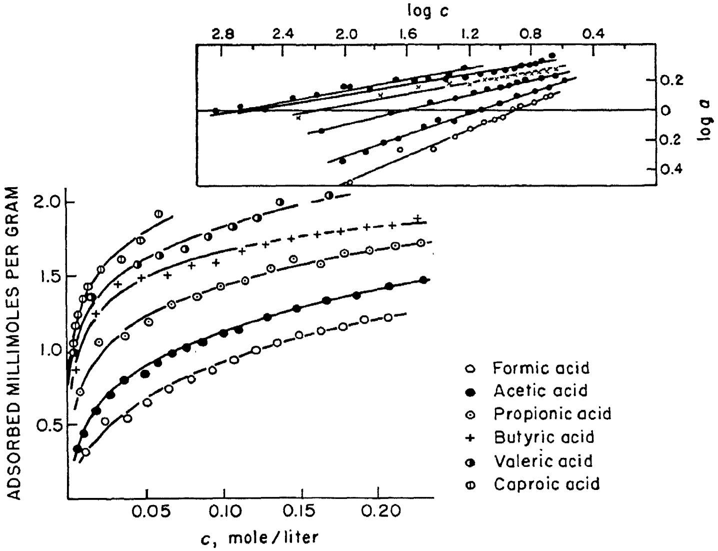

Fig. IV-1. Adsorption isotherms for the homologous series of fatty acids from water onto Norit charcoal. Arithmetic plot below; logarithmic plot above.[38]

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[35] Fowkes and Harkins, *J. Am. Chem. Soc.*, 62, 3377 (1940).
[36] Freundlich, *Z. physik. Chem.*, 57, 385 (1907).

ported by Wöhler and Wenzel.[37] The same order held at 20, 40, 60, and 80°, though adsorption decreased with increase in temperature. Linner and Gortner[38] made an extensive study of the adsorption of organic substances from aqueous solutions on Norit at room temperature (22–30°). Results for the fatty acids are shown in Fig. IV-1. It is evident that Traube's rule was followed. Traube's rule was also found to hold in the adsorption of formic, acetic, and butyric acids from aqueous solution onto a water-insoluble acid-catalyzed phenol-formaldehyde resin.[39]

The rule has been found to hold also in certain cases for adsorption from organic solvents.[40] In extensive experiments Claesson[41] found the order of increasing adsorption on a Carboraffin from absolute ethanol to follow Traube's rule from hexanoic to nonadecanoic acids, inclusive. He also showed [41,42] with a more limited range of acids that the rule holds with six other charcoals. Adsorption of branched-chain acids also followed the rule: isovaleric being more strongly adsorbed than isobutyric acids.[38]

A large number of other studies of adsorption in which Traube's rule was found to hold can be cited. These will not be mentioned, since no advantage would be gained. The literature is very extensive.

Class b. It has been found in many cases that the adsorption of fatty acids from solution to solid surfaces does not follow the order found by Traube for adsorption at the surface of aqueous solutions. Holmes and McKelvey[43] reported the order for adsorption from toluene onto a large-pored silica gel[44] to be caprylic < butyric < propionic < acetic. Bartell and Fu[45] found adsorption from water or carbon tetrachloride to silica gel to be in the order butyric < propionic < acetic < formic, and in all cases to be greater from carbon tetrachloride than from water. Kaufmann[46] observed the order from trichloroethane to silica gel to be stearic < myristic; stearic < lauric; in chromatographic measurements. Cassidy[47] found adsorption from petroleum ether to silica gel to be stearic < lauric. Elder and Springer[48] found the order of adsorption on Patrick's silica gel at 20° to be palmitic $<$ propionic $<$ acetic, from the solvents carbon tetrachloride, toluene, nitrobenzene, dioxane and water. The adsorption decreased, for each acid, in the solvents in the above order. Heymann and Boye[49] adsorbed fatty acids on powdered gold from 0.01 N solutions. The order butyric $<$ propionic $<$ acetic $<$ formic held from carbon tetrachloride, benzene, alcohol, acetone, and water. Caproic acid was less adsorbed than the above four in all but the first solvent, when it fell between propionic and acetic. When adsorptions were ranked on the basis of solvents the order of solvents differed for each acid.

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[37] Wöhler and Wenzel, *Kolloid-Z.*, 53, 273 (1930).

[38] Linner and Gortner, *J. Phys. Chem.*, 39, 35 (1935).

[39] S. S. Bhatnagar, Kapur, and M. S. Bhatnagar, *J. Indian Chem. Soc.*, 16, 261 (1939).

[40] Cassidy, *J. Am. Chem. Soc.*, 62, 3073 (1940).

[41] Claesson, *Arkiv Kemi, Mineral. Geol.*, A23, No. 1 (1946).

[42] Claesson, in *The Svedberg 1884–1944*. Almqvist & Wiksells, Uppsala, 1944, p. 82.

[43] Holmes and McKelvey, *J. Phys. Chem.*, 32, 1522 (1928).

[44] Holmes, Sullivan, and Metcalf, *Ind. Eng. Chem.*, 18, 386 (1926).

[45] Bartell and Fu, *J. Phys. Chem.*, 33, 676 (1929).

[46] Kaufmann, *Fette u. Seifen*, 46, 268 (1939).

[47] Cassidy, *J. Am. Chem. Soc.*, 62, 3073 (1940).

[48] Elder and Springer, *J. Phys. Chem.*, 44, 943 (1940).

S. S. Bhatnagar, Kapur, and M. S. Bhatnagar[50] found a reversal of Traube's rule for adsorption from water on a *m*-phenylenediamine-formaldehyde resin; the order was butyric $<$ acetic $<$ formic acids. These authors[51] also found reversal for adsorption on a resorcinol-formaldehyde ammonia-catalyzed resin from water, but the Traube order held for the resin formed by hydrochloric acid catalysis. All resins gave reversal of the Traube order when the acids were adsorbed from benzene, chloroform, or carbon tetrachloride.

In chromatographic observations, Manunta[52] found the order on magnesium sulfate, or Frankonite, from petroleum ether to be stearic $<$ palmitic. Kaufmann[53] reported the order on alumina from benzene to be myristic $<$ stearic; myristic $<$ palmitic; lauric $<$stearic; lauric $<$ palmitic. In static adsorption experiments from petroleum ether onto "Micron" magnesium oxide the order was lauric $<$ stearic; on an active clay ("Filtrol"), stearic $<$ lauric.[54]

Class c. Cases have been reported in which it was found that all the fatty acids were adsorbed to about the same extent. Thus Cassidy[54] found that on Merck's Brockmann alumina, as well as on another alumina the adsorption isotherms of lauric, myristic, and palmitic acids from light petroleum were identical. On each of four commercial charcoals the isotherms for lauric, palmitic, and stearic acids from petroleum ether lay close together and crossed each other. It must be that in cases such as these the adsorption is so strongly controlled by the carboxylic acid group that any other influence such as solubility is overshadowed. The acids are all adsorbed to about the same molar extent. Heymann and Boye,[49] in the study of adsorption on gold powder, reported that the acids undecylic, myristic, and stearic were virtually unadsorbed from 0.01 *N* solutions in carbon tetrachloride, benzene, alcohol, or acetone. Gyani and Ganguly[55] observed the adsorption from alcoholic solutions onto Patrick's silica gel at 25° to be strong for formic acid, but to be almost the same for the normal acids of carbon content 2, 3, 4, 5, 6, 9, 11, 12, 14, 16, 17, and 18 carbon atoms. The adsorption lay between 52.8 and 60% from the solutions of initial concentration 0.01 *N*. This behavior was related by the authors to adsorption through the carboxylic acid group. Smith and Fuzek[56] measured the specific surfaces of Raney nickel by adsorption of fatty acids from benzene. Essentially the same area was found when capric, lauric, palmitic, nonadecylic, or behenic acids were used.

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[49] Heymann and Boye, *Kolloid-Z.*, 59, 153 (1932).

[50] S. S. Bhatnagar, Kapur, and M. S. Bhatnagar, *J. Indian Chem. Soc.*, 16, 249 (1939).

[51] S. S. Bhatnagar, Kapur, and M. S. Bhatnagar, *J. Indian Chem., Soc.*, 17, 361 (1940).

[52] Manunta, *Helv. Chim. Acta*, 22, 1156 (1939).

[53] Kaufmann, *Fette u. Seifen*, 46, 268 (1939).

[54] Cassidy, *J. Am. Chem. Soc.*, 62, 3073 (1940).

5. Aromatic Carboxylic Acids

The adsorption of benzoic acid and chloro-, nitro-, amino-, and hydroxybenzoic acids from 0.01 *M* alcohol solutions onto Patrick's silica gel was studied by Gyani and Ganguly.[55] They concluded that, in general, the introduction of an active group led to enhanced adsorption over benzoic acid, but that position isomers did not differ much in adsorbability. Sata[57] found the order for adsorption on animal charcoal from water at 20° to be *p*- < *m*- < *o*-hydroxybenzoic acids.

6. Dicarboxylic Acids

Traube[58] found the order of increasing surface activity (by the capillary rise method) to be oxalic, malonic, succinic for equal concentrations in aqueous solutions at 15°. Landt and Knop[59] observed the adsorption on ash-free charcoal to lie in the order oxalic < malonic < succinic < glutaric < adipic from water solution. The same order of adsorption was found from 0.02 *N* hydrochloric acid solution.

A comparison of the adsorptions of the dibasic acids oxalic to adipic from aqueous solutions onto Norit was made by Linner and Gortner.[60] It revealed that some of the curves cross, so that the order of adsorption is different at different concentrations (an example of the danger of generalizations based on data taken over too limited a range). At quite low concentrations the order of increasing extent of adsorption is oxalic, malonic, succinic, glutaric, adipic; at somewhat higher concentration it is oxalic (glutaric, adipic), malonic, succinic. Bhatnagar, Kapur, and Bhatnagar[50] observed the order of increasing extent of adsorption on a *m*-phenylenediamineformaldehyde resin from aqueous solution to be adipic, succinic, malonic, oxalic; the last two isotherms crossed each other. Jain and Jha,[61] using a sugar charcoal carbonized with sulfuric acid, washed, dried, sieved and activated 1 hr. at 800–850°, found the order of adsorption from water to be oxalic $<$ malonic $<$ succinic. For salts the order found was sodium acid oxalate $<$ sodium acid succinate. The log-log curves took a zigzag course. This, the authors thought, indicated a discontinuous adsorption process.

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[55] Gyani and Ganguly, *J. Indian Chem. Soc.*, 20, 331 (1943).

[56] H. A. Smith and Fuzek, *J. Am. Chem. Soc.*, 68, 229 (1946).

[57] Sata, *Kolloid-Z.*, 49, 275 (1929).

[58] Traube, *Ann.*, 265, 27 (1891).

[59] Landt and Knop, *Z. physik. Chem.*, A162, 331 (1932).

[60] Linner and Gortner, *J. Phys. Chem.*, 39, 35 (1935).

Claesson[62] found the Traube order to hold for the dibasic acids adsorbed from absolute ethanol onto Carboraffin CIV, the order of increasing extent of adsorption at a given concentration (dilute solutions) being hexanedioic, octanedioic, nonanedioic, decanedioic, dodecanedioic. Adsorption from aqueous 0.01 and 0.1 *N* solutions on silica gel was found by Bartell and Fu[63] to be small for succinic acid and zero for oxalic. Gyani and Ganguly[64] reported adsorption on Patrick's silica gel at 25° from 0.01 *M* alcohol solution to be adipic $<$ glutaric $<$ succinic $<$ malonic $<$ oxalic, *i.e.*, the Traube order was reversed. The authors suggest that the molecules lie flat on the surface at low concentrations. At higher concentrations (0.05 and 0.1 *M*) the adsorptions of succinic, glutaric, and adipic were equal, indicating to these investigators that the molecules were vertically oriented, with one carboxylic group on the surface.

Isomeric dicarboxylic acids have been the objects of many studies. Traube[65] found the order of increasing surface activity at equal concentrations of the aqueous solutions at 15° to be maleic, fumaric. The relative adsorbabilities of isomeric cyclohexanedicarboxylic acids from water solution onto Merck's *carbo medicinalis* were compared by Kuhn and Wasserman.[66] (The adsorbent had been extracted with alcohol, washed, and dried *in vacuo* to constant weight. It contained 10% moisture and 5.9% ash. The experiments were done on a micro scale with an accuracy estimated at 1%.) The results are shown in Table IV-2.

The order of increasing adsorption onto Norit from water solution was found by Linner and Gortner[67] to be maleic, fumaric. For another set of

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[61] Jain and Jha, *J. Indian Chem. Soc.*, 17, 685 (1940); 18, 321 (1941).

[62] Claesson, *Arkiv Kemi, Mineral. Geol.*, A23, No. 1 (1946).

[63] Bartell and Fu, *J. Phys. Chem.*, 33, 678 (1929).

[64] Gyani and Ganguly, *J. Indian Chem. Soc.*, 20, 331 (1943).

[65] Traube, *Ann.*, 265, 27 (1891).

[66] Kuhn and Wassermann, *Helv. Chim. Acta*, 11, 70 (1928).

[67] Linner and Gortner, *J. Phys. Chem.*, 39, 35 (1935).

TABLE IV-2

Adsorption of Cyclohexanedicarboxylic Acids on Animal Charcoal from Water Solution[66]

Acid	M.p.	Solubility	K_1[a]	% adsorbed
Ortho				
cis............	190	larger[b]	4.6×10^{-5}	29
trans..........	215	smaller	6.6	24
Meta				
cis............	162	larger[c]	8.0	24
trans..........	147	smaller	4.9	27
Para				
cis............	163	larger[d]	3.6	24
trans........	>300	smaller	6.6	33

[a] K_1 is the first dissociation constant.

[b] Baeyer, *Ann.*, **258**, 169 (1890).

[c] Böeseken and Peek, *Rec. trav. chim.*, **44**, 841 (1925).

[d] Baeyer, *Ann.*, **245**, 173 (1888).

isomers the order was itaconic < citraconic < mesaconic. Sata[68] found the order citraconic < mesaconic for adsorption from water solution at 20° onto Merck *carbo animalis*.

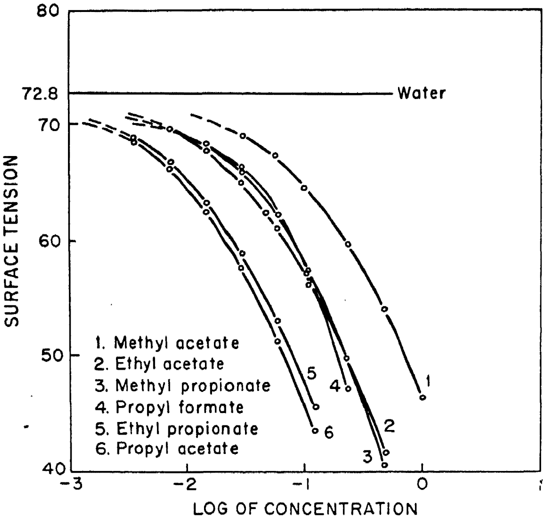

Fig. IV-2. Surface tension–concentration curves for esters in aqueous solutions, recalculated from the data of Traube by King.[69]

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[3] Sata, *Kolloid-Z.*, 49, 275 (1929).

7. Esters

Traube[65] reported the order of adsorption of esters at the aqueous solution–air interface to increase regularly for a given acid residue up the homologous series of alcohols. Surface tension–concentration curves were plotted from Traube's data by King[69] (Fig. IV-2). The curves show the marked influence of chain length on the surface tension lowering; they fall into three groups, the order of adsorption being $C_3 < C_4 < C_5$ esters. Claesson[70] found the order of adsorption on Kahlbaum *carbo activ* from 1% solutions in ether at 20°, using the retardation volume technique, to be trilaurin < triolein < trimyristin < tripalmitin. The adsorption differences were smaller when benzene or chloroform were used as solvents. Kaufmann and Wolf[71] observed the order of adsorption on alumina and

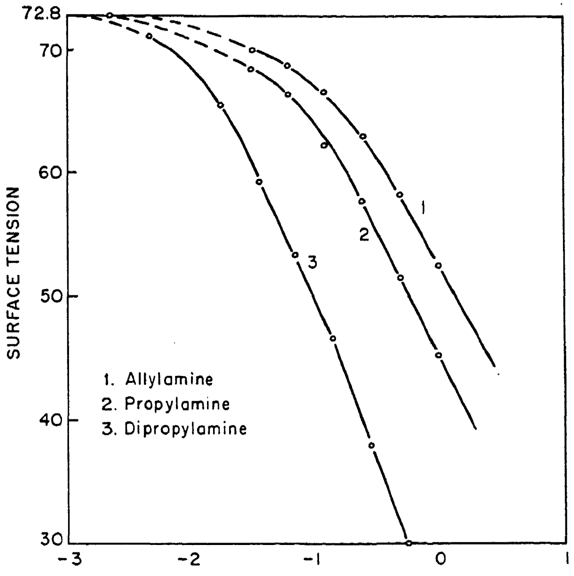

Fig. IV-3. Surface tension–concentration curves for several amines in aqueous solutions.

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[69] King, Kansas Agr. Expt. Sta., *Tech. Bull.* 9 (1922).

[70] Claesson, *Arkiv Kemi, Mineral. Geol.,* A15, No. 9 (1942).

[71] Kaufmann and Wolf, *Fette u. Seifen,* 50, 519 (1943).

silica gel, by a chromatographic technique, to be tristearin $<$ tributyrin. On these adsorbents the order tri- $<$ di- $<$ monostearin was observed.

Kirschner, Prater, and Haagen-Smit[72] separated the *p*-phenylphenacyl derivatives of fatty acids in 1:1 benzene-ligroin solution on Merck's silicic acid. The order of adsorption in the chromatogram was higher molecular weight $<$ lower molecular weight derivative. The binary mixtures investigated were derivatives of acetic to caproic, inclusive, and isobutyric, isovaleric, isocaproic, each from the next higher or lower in the series.

8. Amines

The Traube rule was found to hold for adsorption of some amines at the surface of aqueous solutions.[65] King recalculated Traube's data for allyl and propyl amines to a weight-molar basis and added the curve for dipropylamine. These curves are shown in Figure IV-3[69] (page 121).

9. Amino Acids

Much work has been carried out on the amino acids in chromatographic applications, especially in connection with exchange adsorption. Results from chromatographic separations may not necessarily reflect the equilibrium order of adsorption of the individual substances (Chapter VIII).

Abderhalden and Fodor[73] found *l*-leucine less strongly adsorbed on charcoal from water than glycyl-*l*-leucine. Earlier work[74] indicated that some adsorbents such as kieselguhr, gum mastic, and kaolin did not adsorb glycine or alanine to any extent. Merck *carbo animalis* adsorbed glycine, *d*-alanine, and *l*-leucine increasingly in this order. The extent of adsorption was not appreciably affected by the acidity of the solution, nor by the optical rotation of the amino acid, but was affected by the presence of salts and of other amino acids or derivatives. These results have been extended by numerous workers[75] and in general it has been shown that adsorption on charcoals from aqueous solutions increased with increase in chain length of the amino acids. Other adsorbents such as fuller's earths, silica gels, aluminas, and various inorganic substances, synthetic resins and exchange adsorbents, have also been studied. Some results are given below. Tiselius[76] reported the order of adsorption on *carbo activ,* Kahlbaum, from 0.5% aqueous solution, by frontal analysis, to be glycine $<$

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[72] Kirchner, Prater, and Haagen-Smit, *Ind. Eng. Chem., Anal. Ed.,* 18, 31 (1946).

[73] Abderhalden and Fodor, *Kolloid-Z.,* 27, 49 (1920).

[74] Abderhalden and Fodor, *Fermentforsch.,* 2, 74, 211 (1917–1918).

[75] Wachtel and Cassidy, *J. Am. Chem. Soc.,* 65, 665 (1943). Block, *Chem. Revs.,* 38, 501, 1946. Cannan, *Ann. N. Y. Acad. Sci.,* 47, 135 (1946).

[76] Tiselius, *Science,* 94, 145 (1941).

alanine < hydroxyproline < asparagine < betaine < proline < valine < leucine < isoleucine < histidine hydrochloride < leucylglycylglycine < arginine < phenylalanine < tryptophan. On Epoint 3n (Lurgi G.m.b.H) at *p*H 3, the order aspartic < glutamic was found, and at *p*H 9.9, ornithine < lysine < histidine < arginine. Cheldelin and Williams[77] found the order of adsorption on Darco G-60 charcoal from water to be glycine < alanine. For this charcoal Wachtel and Cassidy[78] found the order glycine < leucine ≪ phenylalanine < tyrosine.

10. Carbohydrates

Considerable chromatographic work has been done with carbohydrates. This has been reviewed by Binkley and Wolfrom.[79] Amiot[80] found the order of adsorption from aqueous solutions on charcoal to be glycerol < glucose < mannitol < saccharose < raffinose. No experimental details were given. Tiselius[76] found the order by frontal analysis at a concentration of 1% in water to be sodium chloride < glucose < lactose. With Hahn[81] he found the order on Carboraffin *C* from water to be saccharose < maltose < raffinose < phenol < ephedrine.

Baum and Broda[82] adsorbed acetylated sugars and cellulose on aluminum oxide and charcoal from a given initial concentration. Octaacetyl cellobiose was less well adsorbed than pentaacetyl glucose on alumina even after an equilibration period of five months. The two were adsorbed on charcoal to an equal extent. Of triacetylcelluloses of three viscosities the order of adsorption on alumina was high viscosity < medium < low viscosity, and the order after five months remained the same, though the adsorption increased. The order on charcoal was high < low < medium. At the end of five months the adsorption had increased, but the order remained the same.

11. Lipids, etc.

Trappe[83] found that most lipoid fractions were weakly or not at all adsorbed from chloroform on Brockmann alumina, while free fatty acids and phosphatides were strongly adsorbed.

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[77] Cheldelin and Williams, *J. Am. Chem. Soc.*, 64, 1513 (1942).

[78] Wachtel and Cassidy, *J. Am. Chem. Soc.*, 65, 665 (1943).

[79] Binkley and Wolfrom, "Chromatography of Sugars and Related Substances," *Sci. Rept. No. 10,* Sugar Research Foundation, New York, 1948.

[80] Amiot, *Compt. rend.*, 208, 1575 (1939).

[81] Tiselius and Hahn, *Kolloid-Z.*, 105, 177 (1943).

[82] Baum and Broda, *Trans. Faraday Soc.*, 34, 797 (1938).

[83] Trappe, *Biochem. Z.*, 307, 97 (1941).

12. Corresponding and Related Compounds

In comparing extents of adsorption up to this point attention has been centered mostly upon homologs and isomers within each functional type. This section brings together a few comparisons between functional types. Corresponding compounds would be those with the same number of carbon atoms but with different functional groups. It will be possible to classify these data in only a rather general way. The literature on this subject is vast.

Fowkes and Harkins[84] found from surface tension and contact angle measurements that adsorption at the air–aqueous solution and paraffin–aqueous solution interfaces are about the same, and that *n*-butylamine is less adsorbed than *n*-butyric acid, which is less adsorbed than *n*-butyl alcohol, though some curves cross. Adsorption at aqueous solution–talc and aqueous solution–graphite interfaces is about the same. The order is *n*-butyl alcohol < *n*-butylamine. Heats of immersion at 25° in calories per gram of powder were found by Boyd and Harkins[85] to be in the orders: for TiO_2, benzene < nitrobenzene < butanol < ethyl acetate < butyric acid < ethanol; for SiO_2, butanol < ethyl acetate < ethanol; for SnO_2, benzene < nitrobenzene < butanol < ethyl acetate; for ZrO_2, nitrobenzene < benzene; for $ZrSiO_4$, benzene < nitrobenzene.

Gyani and Ganguly[86] found the order of adsorption from alcoholic solution at 0.01 *M* initial concentration onto Patrick's silica gel at 25° o be propionic < lactic; succinic < malic < *dl*-tartaric; benzoic < *m*-hydroxybenzoic < *o*-hydroxybenzoic acid; naphthoic < 2-hydroxynaphthoic; phenylacetic < mandelic. Thus, substitution of an H by an OH in the molecule always increased the adsorption, but the amount of increase was not a constant. These results were the reverse of those of Schilow and Nekrassow[87] for adsorption onto medicinal charcoal from aqueous solutions.

Freundlich and Masius[88] adsorbed acids on acid-purified blood charcoal (Merck) and observed the order oxalic < succinic < benzoic. Guyani and Ganguly[89] found for adsorption from 0.01 *M* alcoholic solutions onto Patrick's silica gel, the order dibromosuccinic < succinic < malic < *dl*-tartaric < *l*-tartaric < *meso*-tartaric.

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[84] Fowkes and Harkins, *J. Am. Chem. Soc.*, 62, 3377 (1940).

[85] Boyd and Harkins, *J. Am. Chem. Soc.*, 64, 1190 (1942).

[86] Gyani and Ganguly, *J. Indian Chem. Soc.*, 20, 331 (1943).

[87] Schilow and Nekrassow, *Z. physik. Chem.*, 130, 65 (1927).

[88] Freundlich and Masius, *Van Bemmelen Gedenkboek*, 1910, 88.

[89] Gyani and Ganguly, *J. Indian Chem. Soc.*, 20, 331 (1493).

Linner and Gortner[90] adsorbed acids from water solution onto Norit (1.25% ash) at room temperature. Orders of adsorption found were: glycolic < acetic; oxalic < acetic < glyoxylic; glyceric nearly equal to lactic < pyruvic < propionic; citric < adipic < caproic; at 0.5 mole/liter equilibrium concentration, acetic < glyoxylic < levulinic < pyruvic < propionic < valeric, while at 0.1 mole/liter, approximately, acetic < levulinic < pyruvic < glyoxylic <propionic < valeric; tartaric < malic < monobromosuccinic nearly equal to dibromosuccinic (curves cross) < succinic; maleic < succinic < fumaric; methylsuccinic < itaconic < citraconic < mesaconic. They report Freundlich and Langmuir isotherm constants for thirty acids. Cheldelin and Williams[91] reported the Freundlich adsorption isotherm constants ($1/n$ and k) for thirty-three amino acids, vitamins, and related compounds on Darco G-60 charcoal.

Many aromatic substances have been compared in attempts to find correlations between extent of adsorption and structure. Patrick and Jones[92] found the order of adsorption from kerosene to silica gel to be benzene < nitrobenzene. Sata,[93] in studies of the adsorption from water to Merck *carbo animalis,* found the order cyclohexanedione < citraconic < mesaconic < hydroquinone < quinone < *p*- < *m*- < *o*-hydroxybenzoic acids. Sata and Kurano[94] found that, in general, the order of adsorption from benzene was dinitrobenzenes < nitranilines < nitrophenols, and from chloroform, dinitrobenzenes < nitranilines. Within the series the order from benzene was *p*- < *o*- < *m*-dinitrobenzenes; *m*- < *o*- < *p*-nitranilines; *m*- < *p*-nitrophenols. From chloroform the order found was *p*- < *o*-dinitrobenzene, the *m*-curve cutting both; and *o*- < *m*-nitraniline. From acetone the order was *o*- < *p*-dinitrobenzenes, the *m*-isotherm cutting the *p*-; *m*- < *o*- < *p*-nitranilines; *m*- < *p*-nitrophenols. Heymann and Boye[95] found the adsorption of benzene less than of nitrobenzene from hexane at low concentration, and both more strongly adsorbed than hexane, onto ash-free wood charcoal in the absence of water. Hexane was adsorbed at low concentrations less from benzene than from nitrobenzene. From chloroform the order of adsorption at low concentrations was amyl < butyl < ethyl < methyl alcohols, and at low concentrations in the alcohol the chloroform was adsorbed least from butyl, most from methyl alcohol, in the order butyl < amyl < ethyl < methyl. The adsorption of benzoic acid was found to increase from one solvent to the other in the order acetone $\ll$ water; acetone $<$ ethyl alcohol; chloroform $<$ ethyl alcohol (though there was not much difference between the two); acetone $<$ chloroform; nitrobenzene $<$ ethyl alcohol; nitrobenzene $<$ acetone. The over-all order was approximately: nitrobenzene $<$ acetone $<$ chloroform $<$ ethyl alcohol $<$ water. Other comparisons can be derived from Table III-3.

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[90] Linner and Gortner, *J. Phys. Chem.,* 39, 35 (1935).

[91] Cheldelin and Williams, *J. Am. Chem. Soc.,* 64, 1513 (1942).

[92] Patrick and Jones, *J. Phys. Chem.,* 29, 1 (1925).

[93] Sata, *Kolloid-Z.,* 49, 275 (1929).

[94] Sata and Kurano, *Kolloid-Z.,* 60, 137 (1932).

[95] Heymann and Boye, *Kolloid-Z.,* 63, 154 (1933).

13. Relation between Structure and Adsorbability. Summary

It is evident, even though the data are, in many respects, inadequate, that within a given homologous series there is usually an order of relative extent of adsorption (from a given solvent to a given surface) which supports the concept of homology. That is, usually there is no haphazard arrangement of the substances when the relative extents of adsorption are compared, but adsorption either increases or decreases in a regular manner with increasing number of CH_2 groups. If a very irregular arrangement were to be observed it would throw some question on the techniques employed in the experiment and cry for verification.

Whether the observed order follows the Traube rule, adsorption increasing regularly and strongly with number of carbon atoms, or is the reverse of the Traube rule, or is not variable with number of carbon atoms, seems not to be solely a function of the chemical structure of the adsorptive, but rather to depend upon the adsorptive-surface interactions, and to be influenced by the solvent. Thus it may be recalled[96] that from petroleum ether the order of adsorption on a charcoal is lauric $<$ myristic $<$ palmitic $<$ stearic acids; on an alumina, lauric $=$ myristic $=$ palmitic; and on a silica gel stearic $<$ lauric acid.

The observed extents of adsorption between substances belonging to different homologous series are of course functions of the chemical structures as long as a given solvent and adsorbent are compared. This is shown in the extensive study of Linner and Gortner[97] in which fatty and substituted acids were adsorbed from water onto Norit charcoal. The authors concluded that under these conditions the introduction of OH into an organic acid decreased its adsorption to an extent depending upon the acid, and NH_2 produced a still greater effect. This is understandable on the basis that OH will increase the interaction with the water. Also, when substituted in the *alpha* position, OH increases acid dissociation. Either of these effects will lessen the tendency toward escape from the solution to the surface. The NH_2 being still more basic than the OH forms a cation NH_3^+ even in water solution, and the zwitterion formed with the carboxyl shows great solubility in most cases compared with the unsubstituted acid. A second OH group further decreases adsorption, but not to the same extent that the introduction of the first OH did. Thus the observed extents of adsorption are glyceric $<$ lactic $\ll$ propionic, and tartaric $<$ malic $\ll$ succinic. The introduction of a keto group tends to decrease the relative adsorption; the orders found for extent of adsorption are pyruvic $<$ propionic; levulinic (γ-ketovaleric) $<$ valeric acid. That glyoxylic acid is more strongly adsorbed than acetic does not seem to fit here; it may indicate that some depolarizing effect occurs in glyoxylic acid. The keto groups would be expected to interact through hydrogen bonding with the water and so lessen the tendency of the adsorptive to escape from the solution. In each case the position of the substituent relative to the carboxylic group must also influence the extent of the adsorption.

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[96] Cassidy, *J. Am. Chem. Soc.*, 62, 3073 (1940).

[97] Linner and Gortner, *J. Phys. Chem.*, 39, 35 (1935).

Introduction of a double bond was shown to increase adsorption in some cases. Orders of adsorption found were methylsuccinic $<$ itaconic $<$ citraconic $<$ mesaconic acids; maleic $<$ succinic $<$ fumaric acids. Introduction of halogen should have an effect similar to, but less marked than, introduction of OH. This is shown in the order tartaric $<$ malic $<$ dibromosuccinic (nearly equal to monobromosuccinic) $<$ succinic acid. In general it might be expected, then, that for substituted aliphatic acids the adsorption from water to charcoal would be, in terms of the substituent groups, $F < Cl < Br < I < OCH_3 < C_6H_5 < H < CH_3$, other things being equal, for acids with substituents on the same carbon atom. This is the order of decreasing "negativity" of the groups as judged by the effect on the dissociation constant of the acid. However, this does not mean that the effect of the substituent is solely related to its effect on the dissociation of the carboxyl group, since geometric and other effects must also influence the adsorption.

A second generalization may be made that, other things being equal, introduction of a negative group should increase the extent of adsorption of the substance from a nonpolar solvent. The data of Heymann and Boye[98] generally bear this out.

There appears to be no good evidence to show that a quantitative relationship can be deduced at present between extent of adsorption at the solid–solution interface, and molecular structure. Evidence is good, however, that certain limited, contingent, qualitative statements such as those above, can be made.[99] At the solution–vapor interface, Traube's rule correlates adsorption with structure *within* the homologous series.

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[98] Heymann and Boye, *Kolloid-Z.*, **63**, 154 (1933).

[99] See LeRosen, Monaghan, Rivet, and E. D. Smith, *Symposium on Adsorption*, Div. Petroleum Chemistry, Atlantic City, Sept. 1949, p. 179; E. D. Smith and LeRosen, *ibid.*, p. 185.

III. ADSORPTION AND MOLECULAR WEIGHT

If relative adsorption changes in a regular way along an homologous series, then there should be a correlation with the molecular weights of the adsorptives. Such a correlation is implied in Traube's rule and has been suggested in other connections. For example, Bakr and McBain[100] adsorbed toluene and acetic acid on sugar charcoal and on extracted charcoal, and found that the ratio between the saturation values for these substances adsorbed from the vapors was that of the molecular weights, the acetic acid being taken as double molecules.

IV. ADSORPTION AND MELTING POINT

It might be expected from an application of general rules that, other things being equal, of two somewhat similar compounds the one with the lower melting point will be the more soluble.[101] Since, other things being equal, the more soluble substance will be less well adsorbed, then a relation should be found between extent of adsorption from solution and the melting point of the adsorptive.

TABLE IV-3

Relation between Structure, Melting Point, Color, Solubility, and Relative Extent of Adsorption of Diphenylpolyenes

No.	Compound[a]	Melting point, °C.	Solubility in g./liter	
			In benzene	In chloroform
1	ϕ—CH=CH—ϕ	124	102.12	153.2
2	ϕ—(CH=CH)$_2$—ϕ	152.5	66.15	97.8
3	ϕ—(CH=CH)$_3$—ϕ	200	8.60	21.4
4	ϕ—(CH=CH)$_4$—ϕ	232	1.20	2.95

The absorption of light (3 maxima) is shifted to longer wavelengths from 1 through 4. The order of relative extents of adsorption is $1 < 2 < 3 < 4$.[b]

[a] Data from Kuhn and Winterstein, *Helv. Chim. Acta,* 11, 87 (1928).

[b] Data from Winterstein and Schön, *Z. physiol. Chem.,* 230, 146 (1934).

A good case can be made that from relatively nonpolar solvents to relatively nonpolar surfaces the higher melting of two substances will be the more strongly adsorbed. Such a correlation is supported by the data in Table IV-3. The correlation can easily be overworked, however, and requires judicious use. The relative adsorbabilities of *cis-* and *trans-*

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[100] Bakr and McBain, *J. Am. Chem. Soc.,* 46, 2718 (1924).

[101] J. H. Hildebrand, *Solubility of Non-electrolytes.* 2nd ed., Reinhold, New York, 1936, p. 35.

azobenzenes (Table IV-4) follow the melting point rule in a nonpolar solvent, but not in polar solvents.

The melting point is characteristic of the solid state of the substance. If the adsorbed film should be "solid" or oriented, then a correlation between relative extent of the adsorption and the melting point of the absorptive might be noticeable. Linner and Gortner[102] found alternation between the values for Langmuir's constant β (Chap. II, Eq. 2) for odd and even homologous monocarboxylic acids, and for dicarboxylic acids. The constant β represents the amount of substance that would be adsorbed if the surface were saturated. The alternation of β was therefore taken to support the notion that the fatty acids were adsorbed in oriented films, in which the even-odd alternation of packing would be displayed.

TABLE IV-4

Relation between Melting Point, Solubility, and Adsorbability of the *cis-* and *trans-*Azobenzenes

No.	Compound[a]	Melting point, °C.	Solubility, millimoles/liter Petr. ether at 0°	Water at 25°	Methanol at 0°
1	*trans*-Azobenzene	68	192	0.02	164
2	*cis*-Azobenzene	71.4	49.4	0.65	410

Order of adsorption on alumina from petroleum ether 1 < 2.[b] Order of adsorption on Norit charcoal from water 2 < 1; from methanol, 2 < 1.[c]

[a] Hartley, *J. Chem. Soc.*, 1938, 633.

[b] Zechmeister, Frehden, and Jörgensen, *Naturwiss.*, 26, 495 (1938).

[c] Freundlich and Heller, *J. Am. Chem. Soc.*, 61, 2228 (1939).

V. ADSORPTION AND SHAPES OF MOLECULES

It is difficult in many cases to differentiate adsorption effects ascribable to molecular shapes from those due to size (or volume). One might think of shape factors as applying in the comparison of the properties of a linear molecule such as 1-hexanol with the more compact cyclohexanol. However, Langmuir[103] showed that the hydrocarbon chain portion of such a "linear" molecule as hexanol must be to some extent curled up when the molecule is in solution so as to offer to the solvent the minimum surface area. Treloar[104] has concluded that in its most probable shape a hydrocarbon molecule is spheroidal, and Ward[105] has extended these ideas to the shapes of small polar molecules (of fatty acids) in surfaces of their solutions. In such cases, therefore, differences in adsorbability may not readily be ascribable to shape if both molecules take the form of a somewhat flattened sphere in the surface. However, as Ward[105] has pointed out, although in solution surrounded by like molecules, the shape is determined solely by configurational probability, the most probable shape approximating a spheroid; in the surface both entropy and surface energy factors influence the shape. At an immobile interface topological factors may be very important also. In this connection it may be recalled that although *n*-hexane is more strongly adsorbed on silica gel than is cyclohexane, the difference in extent of adsorption between the two is small.[106] When branched-chain molecules are compared with each other, and with *normal* molecules, then some of the differences observed may be ascribable to shape. Thus, Weber and Sternglanz[107] found that among lower aliphatic alcohols those with normal chains are more capillary active in the surface of their water solutions than those with branched chains. Of isomers with branched chains, those with the branching farthest from the polar OH group are more surface active. Unsymmetrical are more active than symmetrical isomers and the surface activity increases from tertiary to secondary to primary compounds.

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[102] Linner and Gortner, *J. Phys. Chem.*, 39, 35 (1935).

[103] Langmuir, in J. Alexander, ed., *Colloid Chemistry.* Vol. I, Reinhold, New York, 1926, p. 525.

[104] Treloar, *Proc. Phys. Soc. London,* 55, 345 (1943). W. J. Taylor, *J. Chem Phys.*, 15, 412 (1947); 16, 257 (1948).

In cases of adsorption from solution to solid surfaces where different classes of molecules are compared, differences in extent of adsorption which are laid to differences in shape[108] need to be scrutinized. Too little is known about the shapes of molecules.[109] In those cases, however, where molecules are constrained to a surface of a homogenous substrate, and are oriented in a deducible manner, there has been obtained good evidence that shape may play an important role in relative adsorption. The subject is discussed by Adam[110] in connection with films of insoluble substances on the surfaces of liquids.

It is understandable that molecular volume may influence adsorption in important but unforseeable ways.[111] Thus it might be expected that in mixtures of carbon tetrachloride and benzene (for example), and because their molecular volumes are nearly the same, the adsorption curve over the entire concentration range should be symmetrical. Yet the adsorption of carbon tetrachloride is much less than that of benzene.[111] Il'in and Kiselev[112] found, in studies of the heat of wetting of steam-activated, sieved, and dried wood charcoal, that the time for complete wetting increased with the molecular volume of the adsorptive. Baum and Broda[113] found that solutions of acetylated celluloses and sugars did not reach equilibrium with alumina and charcoal even in several months' contact. This was presumably due to the large molecular size of the adsorptives. Bruns[114] concluded that the reversal of Traube's rule, sometimes found for adsorptions on charcoal, was caused by the presence of pores which were not accessible to compounds with large molecular volumes.[115]

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[105] Ward, *Trans. Faraday Soc.*, 42, 399 (1946).

[106] Mair, Gaboriault, and Rossini, *Ind. Eng. Chem.*, 39, 1072 (1947).

[107] Weber and Sternglanz, *Z. physik. Chem.*, A169, 241 (1934).

[108] See, for example, Elder and Springer, *J. Phys. Chem.*, 44, 943 (1940).

[109] Pauling, *Chem. Eng. News*, 24, 1788 (1946).

[110] N. K. Adam, *The Physics and Chemistry of Surfaces*. 2nd ed., Oxford Univ. Press, London 1938, p. 46 ff.

[111] Heymann and Boye, *Kolloid-Z.*, 63, 154 (1933).

That there should be a relation between molecular volume and extent of adsorption would follow on two lines of reasoning. Several workers[116] have pointed out that adsorbability should tend to increase with chain length because of the increase of cohesive forces up the homologous series (for example, as manifested in the regular increase in heat of melting). The apparent molecular volume of a solute in solution should also be correlatable with extent of adsorption through the evidence it gives of the interaction between solute and solvent.[117]

VI. ADSORPTION AND SURFACE TENSION OF THE PURE ADSORPTIVE

That the relative surface tensions of the pure adsorptives might show a correlation, within an homologous series, to relative adsorbabilities from solution would follow, subject to previously discussed qualifications, from the fairly regular manner in which the surface tensions of the liquid members of the given homologous series change with chain length. This regularity can be seen from the data on aliphatic alcohols taken from a paper by Smith and Sorg[118] (Table IV-5) and on hydrocarbons from a paper by Smith[119] (Table IV-6). But such a correlation cannot be expected to be generally useful as between homologous series. These and other data indicate that the value of the surface tension of hydrocarbons, while increasing first rapidly with chain length, then more slowly, approaches a limiting value of about 31 dynes per centimeter, which is the limit approached also, but at shorter chain lengths, by the surface tension values for liquid fatty acids and alcohols. The correlation can only be useful where the adsorption involves predominantly the hydrocarbon portion of the molecule. Where the effect of this portion is negligible, there is no correlation. Thus the interfacial tension between paraffin hydrocarbons and water does not vary with chain length, but remains at 51 dynes per centimeter at 20°.[120] Also, within a group of

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[112] Il'in and Kiselev, *Kolloid-Z.*, 66, 28 (1934).

[113] Baum and Broda, *Trans. Faraday Soc.*, 34, 797 (1938).

[114] Bruns, *Kolloid-Z.*, 54, 33 (1931).

[115] In this connection, see also Nekrassow, *Z. physik. Chem.*, 136, 18, 379 (1928); Landt and Knop, *Z. Elektrochem.*, 37, 645 (1931).

[116] Baum and Broda, *Trans. Faraday Soc.*, 34, 797 (1938); Broda and Mark, *Z. physik. Chem.*, A180, 392 (1937).

[117] Bauer, "Determination of Density," in Weissberger, ed., *Physical Methods of Organic Chemistry*, 2nd ed., Interscience, New York, 1949, Part I, p. 253 ff.

[118] G. W. Smith, and Sorg, *J. Phys. Chem.*, 45, 671 (1941).

[119] G. W. Smith, *J. Phys. Chem.*, 48, 168 (1944).

TABLE IV-5

Properties of Aliphatic Alcohols

Alcohol	B.p.[a]	D[a]	S.T.[a]	C[b]	μ[c]	ϵ[d]
Methanol	64.5	0.790	22.6	—	—	—
Ethanol	78.3	0.786	22.2	—	—	—
1-Propanol	97.8	0.800	23.4	360	1.66	19.3
2-Propanol	82.3	0.783	22.1	410	—	—
1-Butanol	117.8	0.805	24.2	—	1.65	17
2-Butanol	99.3	0.802	23.3	—	—	—
2-Methyl-1-propanol	108.1	0.795	22.3	108	—	—
2-Methyl-2-propanol	82.5	0.779	20.8	—	—	12.6
1-Pentanol	138.2	0.813	25.3	27.0	1.7	14.5
2-Pentanol	119.7	0.830	24.1	42.0	—	—
3-Pentanol	111.6	0.818	24.1	50.0	—	—
3-Methyl-1-butanol	130.3	0.806	23.3	34.0	—	—
3-Methyl-2-butanol	114.1	0.815	23.0	—	—	—
2-Methyl-1-butanol	125.6	0.834	25.1	39.0	—	—
2-Methyl-2-butanol	101.7	0.806	22.4	75.0	—	7
1-Hexanol	155.1	0.816	25.8	—	1.6	—
1-Heptanol	175.5	0.819	27.1	—	1.71	—
1-Octanol	193.7	—	—	—	1.68	10
1-Nonanol	216	0.824	28.1	—	1.6	—
1-Decanol	231	0.827	28.6	—	1.6	8.1
1-Hendecanol	244	0.830	28.9	—	1.66	—
1-Dodecanol	260	0.828	29.6	—	1.62	6.8

[a] B.p., boiling point; D, density; S.T., surface tension in dynes/cm., rearranged from Smith and Sorg.[118]

[b] C, the concentration in millimoles/liter in water required to bring the surface tension to 55 dynes/cm. (capillary rise method), from Weber and Sternglanz, *Z. physik. Chem.*, **A169**, 241 (1934).

[c] μ, dipole moment in debyes, from Ralston, *Fatty Acids and Their Derivatives*, Wiley, New York, 1948.

[d] ϵ, from Girard, *Trans. Faraday Soc.*, **30**, 763 (1923).

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[120] Ward, *Trans. Faraday Soc.*, **42**, 399 (1946).

isomers, there is no correlation to be found (Table IV-5). Among the amyl alcohols the order showing increasing surface tension is different from that showing a regular change (increase or decrease) of capillary activity in water solution.

TABLE IV-6

Surface Tensions of Hydrocarbons at 20° by the Pendant-Drop Method[119]

Hydrocarbon	Surface tension, dynes/cm.
Pentane	16.3
2-Methylbutane	15.5
Heptane	19.7
Octane	21.7
2-Methylheptane	20.7
3-Methylheptane	21.2
4-Methylheptane	21.2
2,5-Dimethylhexane	19.8
2,2,4-Trimethylpentane	18.9
Cyclohexane	25.2
Ethylcyclohexane	25.8
Cyclohexene	26.6
Benzene	29.2
o-Xylene	30.1
p-Xylene	28.5

VII. ADSORPTION AND ASSOCIATION OF THE ADSORPTIVE

Association of the molecules of the adsorptive has been thought to affect the extent of an adsorption. Thus Bakr and McBain,[121] in studying the adsorption of toluene and acetic acid on charcoal from sugar, and on extracted animal charcoal, found acetic acid less adsorbed at high temperatures than toluene. At 245° practically no acetic acid, but considerable toluene was adsorbed. This was related by these authors to the known effect of high temperature in dissociating the acetic acid dimers. Heymann and Boye[122] suggested that the adsorption of benzoic acid from nitrobenzene onto charcoal is greater than that from acetone or nitromethane because the benzoic acid is exceedingly strongly associated in the nitrobenzene.

Certain associations of solute and solvents to form complexes with special adsorption characteristics have been adduced by Doss and B. S.

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[121] Bakr and McBain, *J. Am. Chem. Soc.*, 46, 2718 (1924).

[122] Heymann and Boye, *Z. physik Chem.*, A150, 219 (1930).

Rao,[123] K. S. and B. S. Rao,[124] and N. S. Rao and S. Jatkar[125] to explain the shapes of isotherms of adsorption from binary mixtures over the entire concentration range.

VIII. ADSORPTION AND IONIZATION OF ADSORPTIVE

It seems to be generally found that ionization of an adsorptive decreases its surface activity. This may be because the ion, with its envelope of solvent, is much more soluble than the unionized molecule, and so shows less tendency to escape from the solution. (The diminution of surface activity with ionization is to be expected from electrostatics: any charged particle is repelled from a region of lower dielectric constant.) A nice example of this type of effect is found in the work of Pappenheimer, Lepie, and Wyman, Jr.[126] When the surface tension of aqueous ε-aminocaproic acid is plotted as a function of pH, least lowering is found at the isoelectric point where the amino acid is present largely as a dipolar

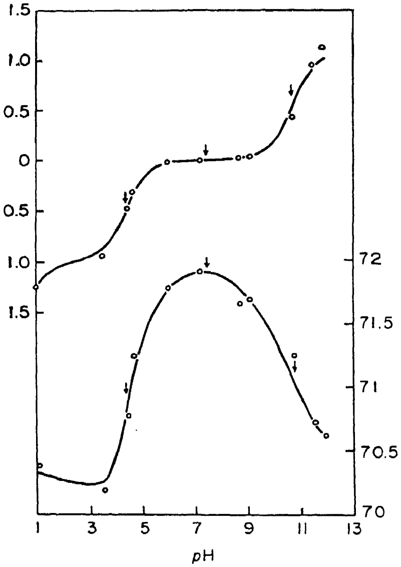

Fig. IV-4. *Lower curve:* surface tension of a 0.2431 *M* solution of ε-aminocaproic acid as a function of pH. *Upper curve:* titration of ε-aminocaproic acid (0.2431 *M*). The ordinates give moles of acid or base per mole of amino acid. The smooth curve is based on pK values of 4.43 and 10.75. The isoelectric point (7.59) and the pK values are indicated by arrows.[126]

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[123] K. S. G. Doss and B. S. Rao, *Half-yearly J. Mysore Univ.*, 8, 49 (1935).

[124] K. S. Rao and B. S. Rao, *Proc. Indian Acad. Sci.*, A4, 562 (1936).

[125] N. S. Rao and Jatkar, *Quart. J. Indian Inst. Sci.*, 5, 65, 72, 80, 87, 91, 98, 103 (1942).

[126] Pappenheimer, Lepie, and Wyman, Jr., *J. Am. Chem. Soc.*, 58, 1851 (1936).

ion (Fig. IV-4). The effect in lowering the surface tension increases on both sides of the isoelectric point where the acid or basic ionizations predominate. Evidently as the amount of monopolar ions increases, whether acidic or basic, the effect of the long hydrocarbon chain becomes felt.[127] The substance in this state behaves like a long-chain compound with a polar head group:

below the isoelectric point: $H_3\overset{+}{N}CH_2CH_2CH_2CH_2CH_2COOH$ (in acid)
above the isoelectric point: $H_2NCH_2CH_2CH_2CH_2CH_2COO^-$ (in base)

It thus becomes, as these structures are more favored by the change in *p*H, more surface active than the dipolar ion.

Many studies have been carried out on the relation between extent of adsorption and degree of ionization. For example, Kuhn and Wassermann[128] indicate that adsorption (of cyclohexanedicarboxylic acids onto animal charcoal from aqueous solution) should be favored by ionic dissociation. No clear evidence for this was found. That equivalent amounts of two ions of an electrolyte are taken up, as shown by analysis, does not necessarily mean that the adsorption is molecular.[129] Evidence is found on both sides of this question. Thus Landt and Knop[130] found the adsorption of the fatty acids acetic through valeric and succinic, glutaric and adipic from water onto ash-free charcoal to be decreased by the presence of 0.02 *N* HCl. The adsorption curve for oxalic acid from HCl crossed that from water, being below it at low concentrations, where the relative amount of HCl was high. Gyani and Ganguly[131] found the adsorption on Patrick's silica gel at 25° from 0.01 *M* alcohol solutions to increase in the order acetic, chloroacetic, dichloroacetic, trichloroacetic; the same order, they point out, as the dissociation constant increases. A clear correlation was not found, however, by Bhatnagar, Kapur, and Bhatnagar[132] for adsorption of these and other acids from water onto basic and acid resins.

The adsorption of acids and bases has been found in some cases to be proportional to the concentration of undissociated molecules.[133] Kolthoff[134] came to the conclusion that the adsorption of strong acids on a certain charcoal was molecular, since capillary-active nonelectrolytes could completely displace the adsorbed acids and since the adsorption was increased by the presence of neutral salts of the acids. Many highly ionized, surface-active substances are known, however, so that the extent of ionization itself cannot be a sole controlling factor.[135]

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[127] Cohn, *Ann. Rev. Biochem.*, 4, 93 (1935).

[128] Kuhn and Wassermann, *Helv. Chim. Acta*, 11, 70 (1928).

[129] Roychoudhury, *J. Indian Chem. Soc.*, 8, 433 (1931).

[130] Landt and Knop, *Z. physik. Chem.*, A162, 331 (1932).

[131] Gyani and Ganguly, *J. Indian Chem. Soc.*, 20, 331 (1943).

[132] S. S. Bhatnagar, Kapur, and M. S. Bhatnagar, *J. Indian Chem. Soc.*, 17, 361 (1940).

[133] Phelps, *Proc. Roy. Soc. London*, A124, 554 (1929); A133, 155 (1931); also E. J. Miller, *Colloid Symposium Monograph*, 5, 55 (1928); Frampton and Gortner, *J. Phys. Chem.*, 41, 567 (1937); Fowkes and Harkins, *J. Am. Chem. Soc.*, 62, 3377 (1940); Fromageot and Wurmser, *Compt. rend.*, 179, 972 (1924).

IX. ADSORPTION AND POLARITY

Polarity as used in connection with adsorption is a rather imprecise term. It usually means a property that depends on electrical dissymmetry, and it may be applied to a molecule as a whole, or to a group in a molecule, or even to a bond.

1. Dipole Moment

Polar molecules are electrically dissymmetric molecules; they would show dipole moments; the larger the dipole moment the more polar the molecule, according to this usage. An order of increasing polarity could then be set up, with corresponding compounds falling, on the whole, in the series *n*-hydrocarbon (0) < ether (1.15) < primary amine (1.3) < alcohol (1.7) < iodide (1.9) < bromide (2.05) < chloride (2.05) < ketone (2.7) < nitro compound (3.4) < nitrile (3.6), among aliphatics, and among benzene derivatives, benzene (0) < diphenyl ether (1.15) < iodobenzene (1.2) < aniline (1.56) < phenol (1.7) < bromobenzene (1.71) < chlorobenzene (1.73) benzophenone (2.95) < nitrobenzene (4.23) < benzonitrile (4.37). In these lists the dipole moments (μ) have been given in debye units (10^{-18} e.s.u. × cm.) in parentheses after each type of compound.

According to this usage *p*-dichlorobenzene would not be a polar molecule, since its dipole moment is 0; nor would be *p*-dinitrobenzene. Also, the lower aliphatic alcohols would all show about the same polarity, since their dipole moments are nearly the same (about 1.7 debye units); and so would the members, except for the first ones, of each of the other homologous series listed above. Another characteristic of the dipole moment is that it does not directly indicate the direction of the electron shift in the dipole.

Group moments[136] may be derived on the definition that C—H, as found in benzene, for example, has no moment, whence the following series can be set up for functional groups attached to carbon: $-\mathrm{NH_2}$ (+1.5); $-\mathrm{CH_3}$ (0.4); —H (0.0); —Cl (−1.5); —OH (−1.7); —CN (−3.8); $-\mathrm{NO_2}$ (−3.9). Here the sign before the figure indicates which end of the dipole is formed by the functional group, *i.e.*, the primary amine dipole and the phenolic dipole would be polarized as shown in the following:

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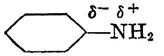
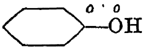
[134] Kolthoff, *Z. Elektrochem.*, 33, 497 (1927).

[135] Anson *et al.*, "Surface Active Agents," R. W. Miner, ed., *Ann N. Y. Acad. Sci.*, 46, 347–530 (1946). A. M. Schwartz and J. W. Perry, *Surface Active Agents*, Interscience, New York, 1949.

[136] Williams, J. W., *J. Am. Chem. Soc.*, 50, 2350 (1928).



and



Bond moments have been derived by Eucken and Meyer[137] and others. A series of these are given below, with the more electronegative member of the pair of bonded atoms written on the right: H—C (0.4); C—O (0.8); C—Cl (1.5); H—O (1.5); C═O (2.3). The relative polarities of bonds can be judged on the relative percents ionic character of the bonds.[138] In general, bonds will manifest polarity in the order covalent < coordinate < ionic, though other factors may influence the actual values. A few data on percents ionic character are given below; they represent the relative contribution of the ionic structure to the resonance hybrid: C—N (6%); C—H (8%); S—H (11%); C—O (12%); C—I (12%); C—Br (15%); C—Cl (18%); N—H (27%); O—H (33%); C═O (47%); C≡N (57%). These values are approximate and the concept is subject to revision. The ionic character of the bond may be influenced by neighboring groups. This subject is discussed by Pauling[138] and others.[139] An estimate of the relative polarity of a linkage may be made on the positions of the linked atoms in the Periodic Table and on their states of oxidation. The use of the Periodic Table in judging polarities of bonds is based on the generalizations that the further above and the further to the right in this table one reduced atom is in relation to the other, the greater the polarity of the bond which will be formed, and, usually, position to the right will be of more influence than position above:

C—H < C—N < C—O < C—F
C—I < C—Br < C—Cl < C—F
C—Cl < C—O

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[137] Eucken and Meyer, *Physik. Z.*, 30, 397 (1929).

[138] L. Pauling, *The Nature of the Chemical Bond.* 2nd ed., Cornell Univ. Press, Ithaca, 1942.

[139] A. E. Remick, *Electronic Interpretations of Organic Chemistry,* 2nd. ed., Wiley, New York, 1949. H. B. Watson, *Modern Theories of Organic Chemistry,* 2nd ed., Oxford Univ. Press, London, 1941. G. W. Wheland, *The Theory of Resonance and Its Application to Organic Chemistry,* Wiley, New York, 1944.

If one of the atoms is in an oxidized form the polarity of the bond will be greatly increased:

$$C{-}CH_3 \ll C{-}COOH$$
$$C{-}NH_2 \ll C{-}NO_2$$
$$C{-}SH \ll C{-}SO_3H$$

The *direction* of the dissymmetry of the bond can be judged on the basis of the relative electron-donating or electron-accepting power of the atoms which constitute it. Thus, in the reduced form, nitrogen may be the plus end of a bond with carbon, if its pair of electrons can be shared with carbon; with OH and particularly Cl under similar circumstances both the tendency to share electrons and the relative electronegative behavior, operating in opposite senses, compete.

Many attempts have been made to correlate dipole moment of the adsorptive with adsorbability, or to sort out the part, if any, played by the dipole moment of the molecule. Heymann and Boye[140] looked for such a correlation on the hypothesis that it would be demanded by the electrostatic theory of adsorption,[141] which considers that a dipole in the adsorptive polarizes the lattice of the adsorbent, producing a mirror image of itself and thus an attractive interaction. Sata and Kurano[142] concluded, with others,[143] that the dipole moment of the adsorptive plays no great role in adsorption from solution, but is outweighed by other influences.

Heymann and Boye[144] came to substantially the same conclusion from a study of the adsorption of fatty acids from chloroform, benzene, ethanol, acetone, and water. Arnold[145] attempted to correlate the order of adsorption in chromatography with dipole moment, but the correlation was beset with exceptions. Attempted correlations by Bhatnagar *et al.*[146] suffer from the use of only one point on the isotherms, with no correlations apparent. The orienting forces caused by permanent and induced dipoles are thought by Travers[147] to play a role in physical adsorption.

When molecules are adsorbed it must be rare that a large part of the molecule is in contact with the surface. Molecules are usually adsorbed with some orientation, and with only a small part of the molecule (perhaps the functional group) in contact with the surface. The rest of the molecule must often be some distance away from the surface, and thus probably not of any particular consequence to the surface–adsorptive interaction. On the other hand, this portion of the molecule must engage in, or at least must be in a position to engage in, interactions with the bulk phase. In view of this reasoning it is not surprising that no useful correlation has been found between relative dipole moment and relative extent of adsorption.

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[140] Heymann and Boye, *Z. physik. Chem.*, A150, 219 (1930).

[141] E. Hückel, *Adsorption und Kapillarcondensation*, Akadem. Verlagsgesellschaft, Leipzig, 1928, p. 55. Lorenz and Landé, *Z. anorg. Chem.*, 125, 47 (1922). Wagner, *Physik. Z.*, 25, 474 (1924). Magnus, *Z. physik. Chem.*, 142, 401 (1929).

[142] Sata and Kurano, *Kolloid-Z.*, 60, 137 (1932).

[143] Briegleb, *Z. physik. Chem.*, B10, 205 (1930).

[144] Heymann and Boye, *Kolloid-Z.*, 59, 153 (1932).

[145] Arnold, *J. Am. Chem. Soc.*, 61, 1911 (1939).

[146] S. S. Bhatnagar, Kapur, and M. S. Bhatnagar, *J. Indian Chem. Soc.*, 17, 361 (1940).

[147] Travers, *Chimie et industrie*, 52, 35 (1944).

2. Solubility Behavior

The degree of polarity of a molecule can be judged from the nature of the groups present in it, or of the bonds present, or from the solubility behavior of the substance. On this latter basis a substance is called *hydrophilic* if it is fairly water-soluble. This usually implies a somewhat polar character to the molecule, or the presence of rather polar groups or bonds, or the absence of relatively large nonpolar groups. *Hydrophobic* substances are not appreciably water-soluble, and likely to be nonpolar. Looking at these properties from another point of view, hydrophilic substances are sometimes spoken of as *lipophobic,* or *oleophobic* (oil-insoluble), and hydrophobic as being *lipophilic,* or *oleophilic.* The general terms are *lyophilic* and *lyophobic.*

The term hydrophilic, besides implying water solubility, also may imply water wettability. In any case it implies a polar nature to the substance. If a substance is wetted by water, or swells in water (indicating penetration of its structure by the water molecules) or dissolves in water, then it has some polar character, but absence of these behaviors may not necessarily mean absence of polar character *in the molecules* of the substance. Thus a surface largely composed of CH_3 groups, as in an oriented fatty acid film, may be quite hydrophobic, the hydrophilic end of the molecules being hidden.

In view of these relationships it would be expected that hydrophilic substances would be less well adsorbed from solution in each other than in hydrophobic substances. An adsorbent that is readily wetted by a substance interacts to some degree with that substance and must adsorb it to some extent (Fig. I-5).

3. Dielectric Constant

The dielectric constant is determined by the concentration of polar molecules in unit mass or unit volume of solution. For this reason it should correlate with relative adsorption better than does the dipole moment. Whereas the dipole moment of normal alcohols, for example, is nearly constant over the homologous series, the dielectric constant for normal alcohols shows a regular decrease[148]; this regularity might be brought into correlation with the regularity of Traube rule adsorption (or its reverse). The variation of the dielectric constant as a function of number of carbon atoms in the molecule when compared for primary and tertiary alcohols indicates for the latter, according to Girard,[148] considerable association into nonpolar complexes (Table IV-7). This might be brought into correlation with the capillary activity of these alcohols.

It is of interest to recall that Rothmund[149] found a fair correlation between the solubility of certain solvents in water and their dielectric constants. The order of increasing solubility in water was as shown below;

TABLE IV-7

Dielectric Constants of Alcohols and Relative Extent of Adsorption[a]

Number of carbon atoms	3	4	5	12
ϵ for the primary alcohol	21.8	17.8(25°)	15.8	6.8[b]
	19.3[b]	17[b]	14.5[b]	
ϵ for the iso alcohol	26	18.7	15.3	
ϵ for the tertiary alcohol	—	11.4	11.7	
		12.6[b]	7[b]	2.75[b]

Adsorption at the surface of the aqueous solutions:[c]

tertiary < secondary < primary alcohols

Adsorption from benzene to silica at low concentrations[d]; and from carbon tetrachloride onto wood charcoal:[e]

isoamyl < normal butyl < normal propyl

Adsorption onto animal charcoal from aqueous solutions:[f]

isopropyl < propyl < isobutyl < butyl < isoamyl

[a] From *International Critical Tables* (ϵ at 20°).

[b] Girard, *Trans. Faraday Soc.*, **30**, 763 (1923).

[c] Weber and Sternglanz, *Z. physik. Chem.*, **A169**, 241 (1934).

[d] Bartell and Scheffler, *J. Am. Chem. Soc.*, **53**, 2507 (1931).

[e] Heymann and Boye, *Kolloid-Z.*, **63**, 154 (1933).

[f] Amiot, *Compt. rend.*, **202**, 1852 (1936); **208**, 1575 (1939).

the dielectric constants of representative substances being given in parentheses: hydrocarbons (benzene, 2.26) < carbon bisulfide (2.64) < halogenated hydrocarbons (chloroform, 4.95) < ether (4.36) < aromatic aldehydes < phenol (9) < nitriles < lower aldehydes (acetaldehyde, 21.1; propionaldehyde, 18.5) < lower ketones (acetone, 20.7; methyl

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[148] Girard, *Trans. Faraday Soc.*, **30**, 763 (1923).

[149] Rothmund, *Z. physik. Chem.*, **26**, 433 (1898).

ethyl ketone, 17.8; diethyl ketone, 17.0; acetyl acetone, 26) $<$ lower alcohols (methyl alcohol, 32.5) $<$ lower fatty acids (formic acid, 57) $<$ water (81.7). The two series are, on the whole, in the same order, but without detailed parallelism. At one end of the series, at the middle, and at the other end, the solvents fall into groups, each with about the same order of dielectric constants. However, as Rothmund points out, isobutyric acid (2.60) and furfurol (39.4) fall out of line. It is therefore likely that although a connection exists between relative solubility of two liquids in water and their dielectric constants, other factors must also come into play.

This solubility series also recalls Trappe's "eluotropic series of solvents".[150] This series, in which solvents are arranged in the order of decreasing strengths as eluents, was set up on the basis of relations between solubility of the solvent in water, water in solvent, surface tension, interfacial tension against water, heat of wetting of various adsorbents, dielectric constant, and dipole moment. The data from Trappe[150] are shown in Table IV-8. Some exceptions to the orderly arrangements are present. No correlation is shown with surface tension and dipole moment, but the correlation with dielectric constant is good.

4. Polarizability

The polarizability of a molecule is measured as the ease with which the positive and negative charges in the molecule can be displaced with respect to each other in the presence of an electric field. It is measured in terms of a constant, α, the magnitude of which is related to the deformability of the molecule; α is constant and independent of the temperature only for molecules without a permanent dipole moment, and for which the dielectric constant is a constant. The polarizability may have different values in different directions in an unsymmetrical molecule, in which case α represents a mean value. α has the dimensions of volume; the molar quantity is $\mathbf{P}$, the molar polarization. The polarizability is made up of two parts, a nuclear, or atom, polarizability, α_A, or $\mathbf{P}_A$, and an electron polarizability, α_E, or $\mathbf{P}_E$. The latter can be calculated from the refractive index of the substance for visible light, and usually constitutes the greater part of the measured α or $\mathbf{P}$.

Polarizability increases with increase in the mobility of valence electrons, and thus would increase with, for example, number of conjugated double bonds, or with distance of the valence electrons from the nucleus. Polarizable molecules might be more soluble in solvents with permanent dipoles than in nonpolar solvents, in which case their ease of adsorption

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[150] Trappe, *Biochem. Z.*, **305**, **150** **(1940)**.

TABLE IV-8

Eluotropic Series of Solvents (Trappe)[150]

	Properties										
Solvent	1	2	3	4		6			9	10	11
Water	—	—	—	73	15.3	12.6	30.2		14.6	81.0	1.84
Methyl alcohol	∞	∞	∞	23	15.3	11.0	21.8	27.6	13.4	31.2	1.73
Ethyl alcohol	∞	∞	∞	22	14.7	10.8	17.2	24.5	12.8	25.8	1.72
n-Propyl alcohol	∞	∞	∞	28.6	13.5	10.2	—	—	13.2	22.2	1.65
Acetone	∞	∞	∞	22.6	13.5	8.0	27.3	—	—	21.5	2.79
Ethyl acetate	8.2	3.0	6.3	—	—	—	18.5	—	—	6.1	1.74
Ether	6.8	1.3	9.7	16.5	8.4	5.8	10.5	—	—	4.4	1.14
Chloroform	0.8	0.1	27.7	26.3	8.0	9.0	8.4	15.7	6.2	5.2	0.95
Dichloroethane	—	—	—	—	—	—			—		1.59
Benzene	—	0.06	32.6	28.8	8.1	5.8	4.6	10.8	6.5	2.3	0.08
Toluene	—	0.04	36.0	28.2					6.4	2.3	0.4
Trichloroethylene	—	0.02									
Carbon tetrachloride	—	0.01	43.4	25.7	8.1	1.8	4.6	9.9	4.7	2.2	0.0
Cyclohexane	—	0.01	—	—	—	—	—	—	3.6	2.0	0.2
Petroleum ether	—	0.007	50.4	17.4	3.1	1.2	3.9	7.2	3.6	1.88	0.0

1. Solubility, g. solvent in 100 g. water at 20°.[a]
2. Solubility, g. water in 100 g. solvent at 20°.[a]
3. Interfacial tension with water at 20°, in dynes/cm.[b]
4. Surface tension at 20°, in dynes/cm.[b]
5–9. Heats of wetting by the solvents for quartz[b] (5); clay[b] (6), Floridin[c] (7); alumina[c] (8); silica gel[d] (9).
10. Dielectric constant at 20°.[a]
11. Dipole moment, $\mu \times 10^{18}$.[a]

[a] Landolt-Börnstein, *Phys.-Chem. Tabellen.*

[b] Oppenheimer-Pincussen, *Tabulae Biologicae.*

[c] Gurwitsch, *Kolloid-Z.*, **32**, 80 (1923).

[d] Grimm, Raudenbusch, and Wolff, *Angew. Chem.*, **41**, 104 (1928).

would be lessened. On the other hand, molecules might be more strongly adsorbed by a very polar adsorbent if they were polarizable. This latter case is thoroughly discussed by Heymann and Boye,[151] who point out that the data found for molecules in the gas phase are not applicable to use for molecules in solution because of the strong interactions produced in the condensed state between solvent, solute, and adsorbent. They argue that even in favorable cases such complicated behavior is being dealt with that only qualitative relations can be expected. Adsorption of benzoic, picric, and acetic acids and iodine from a wide variety of solvents onto de-ashed beechwood charcoal yielded results difficult to interpret in terms of dipole and polarizability effects. (For example, the adsorption isotherms crossed.)

Adsorption of benzoic acid (25 cc. 0.01 *N* solution with 2 g. charcoal) and picric acid (25 cc. 0.0033 *N* solution with 1 g. charcoal) from a series of alcohols (methyl, ethyl, propyl, isobutyl, isoamyl, and secondary octyl alcohols) was studied. The alcohols all have nearly the same dipole moment, but their deformability increases with number of carbon atoms. The adsorption of the solvent, expected to increase with molar polarization, and thus with number of carbon atoms, would be reflected by decreasing adsorption of the solutes. This was found to agree with the data:

TABLE IV-9

Relation between Polarizability and Adsorbability[151]

Solvent alcohols	Molar polarization, cc.	Molar refraction	Percent of solute adsorbed	
			Benzoic acid	Picric acid
Methyl	36.8	8.1	82	98
Ethyl	52.1	10.3	72	91
Propyl	65.1	16.9	66	75
Isobutyl	78.8	27.5	62	64
Isoamyl	90.6	31.4	55	50
sec-Octyl	—	40.4 (calc.)	—	41

Adsorption from mixtures of solvents was studied. In mixtures the dielectric properties of the solvent could be changed in a continuous manner. The following results were obtained: with both solvent components nonpolar (carbon tetrachloride–benzene) the molar polarization curve was linear; likewise the adsorption curves for benzoic and picric acids from dilute solutions at a single initial concentration. With one solvent component polar and the other nonpolar (carbon tetrachloride–toluene, benzene–toluene, benzene–chloroform) the molecular polarization curve was nearly linear as were the adsorption curves. In most cases the adsorption was decreased if the molar polarization of the solvent increased.

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[151] Heymann and Boye, *Z. physik. Chem.*, A150, 219 (1930).

With mixtures of polar and nonpolar solvents, where strong mutual influences were at work (benzene–nitrobenzene), or with mixtures of two polar solvents (alcohol–water, alcohol–acetone, alcohol–chloroform) quite complicated curves were obtained showing no clear correlation between the course of the polarization curve and of the adsorption. *One generalization which could be made, however, was that adsorption of the solutes was almost always less from mixed solvents than from pure solvents.*

Arnold[152] attempted to correlate relative intensity of adsorption on alumina (in a chromatogram) with dielectric properties of molecules and concluded that where no permanent dipoles exist in molecules those with higher polarizabilities would be more strongly adsorbed. The diphenylpolyenes were cited as examples (see Table IV-3). Bhatnagar *et al.*[153] found some correlation between polarizability of solute and solvent and adsorption onto polar and nonpolar types of phenol-formaldehyde and amine-formaldehyde resins.

Chromatographic studies of the separation of condensed-ring hydrocarbons[154] indicate that for the same number of rings it is the linearly arranged compounds which are better adsorbed (on alumina). A linear arrangement of the rings imposes a greater "strain" on the bonds, with concomitant appearance of color, than angular junction. Thus, chrysene is less well adsorbed than naphthacene. Comparing the condensed-ring hydrocarbons, the following orders of adsorption were found: benzene < naphthalene < anthracene < naphthacene < 2,3,6,7,-dibenzanthracene; phenanthrene < pyrene < chrysene < 1,2-benzopyrene; anthracene < chrysene; 1,2-benzopyrene < perylene; phenanthrene < anthracene; chrysene < naphthacene. Physical data for some of these hydrocarbons are given by Kronberger and Weiss[155] (Table IV-10). There seems to be

TABLE IV-10. Properties of Certain Aromatic Substances

Compound	M.p.	M	d	ϵ	P_{L}	P_{D}
Naphthalene.........	80	128	1.158	3.07	45.2	76.2
Phenanthrene........	101	178	1.175	3.01	60.7	101.3
Anthracene..........	218	178	1.245	3.46	64.1	116.7
Chrysene............	254	228	1.27	3.32	78.1	138.6

M = molecular weight; d = density; ϵ = dielectric constant (mean); P = molecular polarization (P_{L}, Lorentz-Lorenz; P_{D}, Drude);[155] M.p. = melting point.

Orders of adsorption[154] naphthalene < anthracene; anthracene < chrysene; phenanthrene slightly less than anthracene.

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[152] Arnold, *J. Am. Chem. Soc.*, 61, 1911 (1939).

[153] S. S. Bhatnagar, Kapur, and M. S. Bhatnagar, *J. Ind. Chem. Soc.*, 17, 361 (1940).

[154] Winterstein and Schön, *Z. physiol. Chem.*, 230, 146 (1934). Winterstein, Schön, and Vetter, *ibid.*, 230, 158 (1934).

[155] Kronberger and Weiss, *J. Chem. Soc.*, 1944, 464.

a relation between relative adsorbability and polarizability: the more polarizable the molecule, the more adsorbable under these conditions of adsorption onto alumina from nonpolar solvents.

X. ADSORPTION AND HYDROGEN BONDING ABILITY

Hydrogen bonding ability of an adsorptive has been invoked to explain relative adsorbabilities of substances. The relative extent of adsorption may be conceived to be influenced by hydrogen bonding ability in the following ways:

(*1*) Bonding of the solute with the solvent may be responsible for abnormally large solubility, with concomitantly lower tendency to escape from the solution into an interface.

(*2*) Hydrogen bonding between solute molecules usually results in a depolarization of the molecule, which may or may not militate against adsorption. In the case of gases this associating effect would lead to increased condensability, which would tend to increase relative adsorbability. Depolarization of a substance through chelation would increase its solubility in a nonpolar solvent.

(*3*) Hydrogen bonding with the adsorbent would tend to increase the extent of adsorption.

If the departures from ideal behavior which lead to increased solubility, as observed by Marvel and coworkers[156] and others[157] are caused by hydrogen bonding of the solute with the solvent, then this effect should decrease the adsorption of such solutes from those solvents.[158] Some evidence for this effect might be found in the adsorption of fatty acids from different solvents, or of chloroform or alcohol from different solvents. However the correlations do not seem to be of a striking nature. The anomalous behavior of picric acid in alcohol–acetone solutions observed by Sata and Kurano[159] may be ascribable to hydrogen bond formation. These authors mention that Bills[160] found the specific conductivity of picric acid in acetone to be ten times less than that in propyl alcohol. This could be due to hydrogen bond formation. The dielectric constants of these solvents are nearly the same: acetone, 21.5; propyl alcohol, 22.5. Landee and Johns[161] state that hydrogen bond formation is not influenced to any extent by the dielectric constant of the solvent.

[156] Zellhoefer, Copley, Marvel, *J. Am. Chem. Soc.*, 60, 1337, 2666, 2714 (1938); 61, 3550 (1939); 62, 227 (1940); and later papers from this laboratory.

[157] Landee and Johns, *J. Am. Chem. Soc.*, 63, 2891 (1941).

[158] J. H. Hildebrand. *Solubility of Non-electrolytes*. 2nd ed., Reinhold, New York, 1936.

[159] Sata and Kurano, *Kolloid-Z.*, 65, 283 (1933).

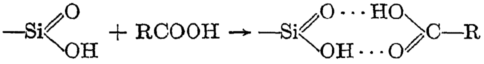
[160] Duff and Bills, *J. Chem. Soc.*, 1931, 1196; 1932, 881.

[161] Landee and Johns, *J. Am. Chem. Soc.*, 63, 2895 (1941).

Hydrogen bonding between or within solute molecules (chelation) might influence relative adsorbability, but no clear evidence of a general correlation appears. The adsorptions of nitrophenols from benzene on alumina and of nitroanilines from petroleum ether onto lime (see above) take the order $o < m < p$; where the chelated, depolarized *ortho* form is least adsorbed. On the other hand the adsorption order for hydroxybenzoic acids onto charcoal from solutions (determined at a single concentration in each case) was: from methyl, ethyl, and *n*-propyl alcohols, $m < p < o$; from ether, $o < m < p$; from acetone, $m < o < p$. No effect of chelation could be observed in adsorptions from mixed solvents.

An interesting suggestion has been made by Volman and Klotz.[162] Certain vapors, which in the liquid state form strong hydrogen bonds, are also more condensable than normal liquids and more adsorbable on charcoal. However, the operation of hydrogen bonding, which at higher partial pressures causes piling up of molecules on the surface, with local condensations, cannot be considered to operate at very low pressure regions of the isotherm, for the molecules are too isolated on the surface.

Elder and Springer[163] have invoked hydrogen bond formation between adsorptives and adsorbent to explain the order of adsorption of certain solutes from given solvents, and, for a given solute, the order of adsorption from different solvents. These authors recall the finding of McGavack and Patrick[164] that silica gel is most adsorptive when it contains about 9% water. They postulate in the silica gel surface structures, such as —SiO(OH), which can bond with the carboxylic acid groups of the organic acids in the manner shown below, thus accounting qualitatively for the adsorption.



$$-\mathrm{Si}\begin{smallmatrix}\nearrow\!\!\!\!\nearrow \mathrm{O}\\ \searrow \mathrm{OH}\end{smallmatrix} + \mathrm{RCOOH} \rightarrow -\mathrm{Si}\begin{smallmatrix}\nearrow\!\!\!\!\nearrow \mathrm{O}\cdots\mathrm{HO}\searrow\\ \searrow \mathrm{OH}\cdots\mathrm{O}\nearrow\!\!\!\!\nearrow\end{smallmatrix}\mathrm{C{-}R}$$

The quantitative agreement is not satisfactory. The order of hydrogen bonding ability which the authors write is palmitic < propionic < acetic < benzoic. The reversal of order of crotonic and propionic found with concentration is difficult to explain. The different effects of solvents with a given adsorptive are thought to be caused by competitions for the surface; the order of increasing adsorption of the solute being that of decreasing ability or tendency of the solvent to form hydrogen bonds with the adsorbent.

Much clearer evidence for the role of hydrogen bonding in adsorption is

[162] Volman and Klotz, *J. Chem. Phys.*, 14, 642 (1946).
[163] Elder and Springer, *J. Phys. Chem.*, 44, 943 (1940).
[164] McGavack and Patrick, *J. Am. Chem. Soc.*, 42, 946 (1920).

found in the binding of water to macromolecular substances. Quantitative studies have been made by Sponsler, Bath, and Ellis[165] and others on the numbers of water molecules which gelatin and other proteins are capable of holding, and of the positions in which they are held. The locations, as shown by x-ray analysis, and the numbers, as obtained from chemical analyses, agree with the evidence of infrared spectrography that the binding is probably through hydrogen bonds. Pauling[166] has interpreted the data for the adsorption of water by proteins to involve initial attachment of one water molecule to each polar amino acid side chain. Two polar side chains may cooperate in the initial process to bind one molecule of water, but, as more water becomes available, further hydration occurs. He also concludes from the data that the normal mutual interaction of peptide carbonyl and imido groups in hydrogen bond formation precludes their active adsorption of water. The adsorption of water by cellulose and other textile fibers may in part be laid to hydrogen bond formation. Magne, Portas, and Wakeham[167] have investigated the subject calorimetrically, and discuss their data and the previous literature. (See also Chapter I.)

XI. SUMMARY

A system can be found, or devised, for almost every molecular property of a group of related adsorptives such that adsorption may be correlated to some extent with that property. In such a system the particular molecular property of the adsorptive is overwhelmingly effective in the adsorption, whether the effect operates directly or indirectly. The correlation found in such a system is usually rather limited and always contingent on other factors. Apart from any theoretical value which it may have, it is often usefully applied in the separation of mixtures of related substances, for here the ambient conditions are the same for all the adsorptives present.

Oftentimes, mixtures of related substances to which these correlations are applicable can be obtained by chemical manipulations from more complex mixtures, as in the separation of acidic and neutral fractions from an hydrolyzate. In such cases the further separation may profitably rest in an adsorption procedure. It was with this in mind that the contents of this chapter were gathered.

With homologous hydrocarbons, adsorption usually increases with increase in molecular weight; for compounds of approximately the same molecular size it usually increases in the order paraffins, cyclanes, olefins (mono-, di-), aromatics condensed-ring aromatics (two-, three-ring compounds); among the condensed-ring aromatics, compounds with rings angularly arranged appear to be less strongly adsorbed than those with a linear arrangement of the rings.

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[165] Sponsler, Bath, and Ellis, *J. Phys. Chem.*, 44, 996 (1940).

[166] Pauling, *J. Am. Chem. Soc.*, 67, 555 (1945).

[167] Magne, Portas, and Wakeham, *J. Am. Chem. Soc.*, 69, 1896 (1947).

Among the lower aliphatic alcohols, Traube's order is usually followed for adsorption from water, and is reversed when the solvent is nonpolar, as is benzene. Too little data are available for the phenols to allow conclusions.

Adsorption of lower aliphatic aldehydes from polar solvents follows the Traube order. However, if the particular polar solvent corresponds to one of the aldehydes, that aldehyde is less well adsorbed than expected and falls out of order in the Traube series.

The aliphatic fatty acids usually follow the Traube order when adsorbed from polar solvents, though many well-established exceptions have been found. The reversal of the Traube order from nonpolar solvents has also shown itself open to many exceptions. The generalization may be made to hold better by considering the nature of the adsorbent. Traube's order usually holds for adsorption of the fatty acids from polar or nonpolar solvents onto relatively nonpolar adsorbents; it is reversed for adsorption from nonpolar solvents onto polar adsorbents. If the adsorbent is strongly basic, all the acids may be adsorbed to the same extent.

In general, the more predominantly polar the substance (weighing the polar part against the nonpolar) the more will it be adsorbed from nonpolar solvents to nonpolar or polar adsorbents, and the less will it be adsorbed from polar solvents. If the substance is nonpolar, then the higher the molecular weight and the higher the unsaturation the greater will be the adsorption. This last generalization emphasizes that in predicting the relative adsorbabilities of two substances not only must the over-all polarity of the molecules be considered but also, and in relation to this, the polarities of solvent and adsorbent.

Such correlations as have been noticed in this chapter leave much to be desired, particularly because of their limited applicability and their generally nonquantitative nature. The reasons for these failings are, however, clear: the extent of adsorption is a function of the natures of the two phases in contact as well as of the adsorptive. Since this is so, the physical properties of the pure adsorptive cannot be expected to correlate with the adsorption, which takes place in a system, unless an extreme situation exists, or unless relative extents of adsorption of two or more related substances are compared for the same solvent and adsorbent.

CHAPTER V

Summary of Relations. Graded Eluents and Adsorbents

I. INTRODUCTION

The following chapters (VI–XI) deal with the use of adsorption to separate mixtures. The mixtures which are ordinarily obtained may consist largely of substances of the same functional type because a chemical fractionation usually precedes the use of physical separation methods. But if the mixtures are complex, and particularly if they are of "natural" origin, it may be impossible to separate out a single functional type by ordinary chemical fractionation. It is therefore necessary in these cases to deal with several functional types in a mixture. Another problem is found in mixtures the molecules of which contain several different functional groups. When adsorption is to be used to separate these mixtures some guides are needed to aid the choice of solvent and adsorbent. The preparation of such guides requires the examination of relations between extent of adsorption and various properties of the system. This examination is made in previous chapters. In this chapter there are gathered and discussed, from a somewhat different point of view, some of the relationships which can be used in connection with Chapters VII to XI.

II. HOMOLOGY

The relation of homology[1] carries with it the implication that the physical properties of the homologs change in a regular manner with increase in the number of carbon atoms in the molecule. This is illustrated for the normal aliphatic alcohols from C_1 to C_9 in Figures V-1 and V-2. Here the values of a number of physical properties are plotted against the number of carbon atoms in the molecule. Excluding the first two members of the series in a few cases, it is evident that the properties change in a regular manner with increase in number of carbon atoms. The characteristic alternation of the melting point is also apparent. It is evident that a qualitative correlation could be made between any of these properties. In those numerous cases, where extent of adsorption from a given solvent to a given surface changes in a regular manner up the homologous series, correlations can be made with any of these properties.

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[1] Senior, *J. Org. Chem.*, 3, 1 (1938–39). R. Locquin, in *Traité de Chimie Organique*, Vol. I, V. Grignard, ed., Masson, Paris, 1935, p. 826.

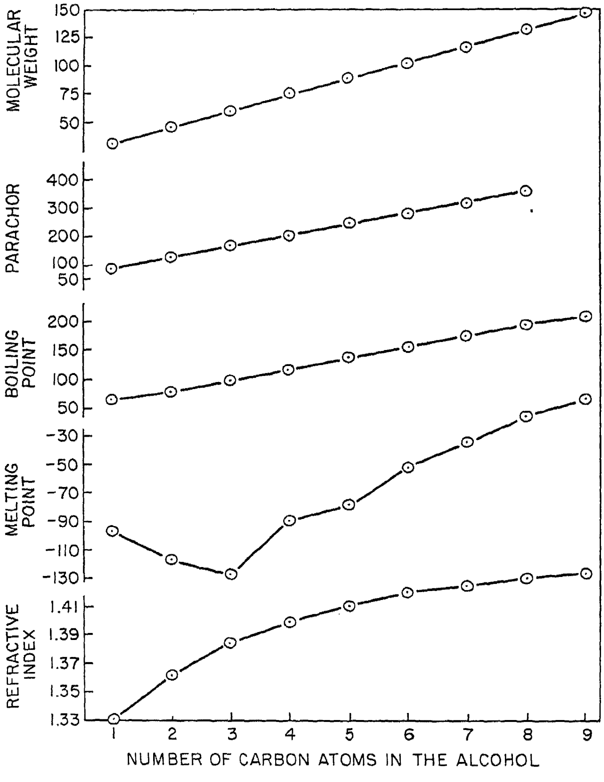

Fig. V-1 Examples of changes in values of some properties along the homologous series of normal alcohols from C_1 to C_9.

Many attempts to make this generalization more quantitative have been made. The Traube rules, and Langmuir's and Taubman's investigations of them belong here, as well as Adam's temperature of half expansion of monolayers, and the other generalizations discussed in previous chapters. In applying adsorption to the separation of mixtures, however, the restricted quantitative rules are not very useful. The relation of homology serves in its applicable realm, as will be described briefly below. But there is needed a relation which does for homologous series what homology does for molecules: a relation which ranks functionally different series, and which could be used to guide all separation methods. Such a relation is not available. The notion of relative polar character serves as a substitute.

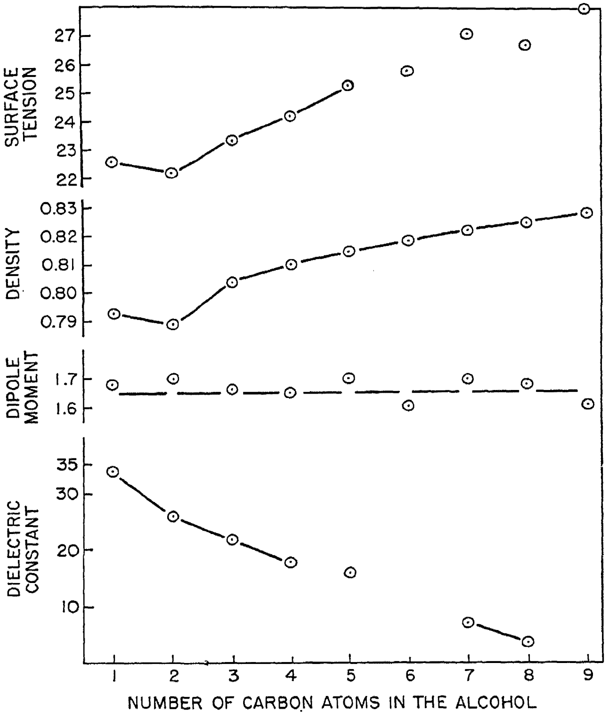

Fig. V-2. Examples of changes in values of some properties along the homologous series of normal alcohols from C_1 to C_9. Density $_{4}^{20}$) (except for C_5, where the value is for d_{20}^{20}).

In adsorption separations the relation of homology is used in choosing adsorbents, separating homologs, and choosing eluents and developers (Chapter VIII). Claesson[2] has suggested that adsorbents may be characterized through one of the constants of the Langmuir adsorption equation. The adsorbents to be compared are tested with two of the homologs to be separated, and the relations between the constants are evaluated. This allows the adsorbents to be ranked on the basis of capacity and separating power. In the separation of homologs, Tiselius' displacement analysis[3] utilizes a more strongly adsorbed homolog to displace a series of less strongly adsorbed ones, which rank themselves in the order of their adsorption (Chapter VIII). As an example, Holman and Hagdahl[4] use a higher fatty acid to displace lower acids, thus the acids from C_6 to C_{10}, dissolved in 50% ethanol–water, could be separated on Darco G-60 charcoal by displacement with the C_{12} acid. In choosing eluent solutions a more strongly adsorbed homolog may be used as an eluent where a less strongly adsorbed one is inadequate. Thus methyl alcohol is more strongly adsorbed to silica gel than butyl alcohol (Table III-3), and would be a better eluent. The first members of homologous series often show differences in properties from the other members. These differences may be exploited under certain circumstances.

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[2] Claesson, *Arkiv Kemi, Mineral. Geol.,* A23, No. 1 (1946).

III. GRADED SERIES OF ELUENTS

1. General Remarks

Eluents* (which also serve as developers) may be ranked in the order of their effectiveness in removing some adsorptive from a given adsorbent. Such ranking can be derived from Chapters III and IV. In many cases the ranking would change with the nature of the adsorptive, and usually would change to some extent with change in adsorbent. Fortunately, however, it has been possible to set up rankings of eluents that hold fairly well over classes of adsorbents. With such series the eluent effect for a given type of adsorptive begins in some region along the series; eluents beyond that point are effective desorbents; substances up to that point are not very effective.

The gradation in behavior of a series of eluents may depend upon the differences between homologs; it may depend upon concentration differences of mixtures; it may depend upon differences in functionality. The differences in the first two cases are largely differences in degree; in the last case they are differences in kind. The most marked differences in eluent activity can be found in series graded because of differences in functional type. Another gradation can be produced by change in temperature. Since adsorption decreases with increase in temperature, then usually the eluent power of a solution would be increased by using it hot.

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* The terms *eluent* and *eluant* are commonly used for a desorption agent. The former seems preferable from an etymological point of view.

[3] Tiselius, *Arkiv Kemi, Mineral. Geol.,* A16, No. 18 (1943).

[4] Holman and Hagdahl, *Arch. Biochem..* 17, 301 (1948); *J. Biol. Chem.* (in press), Hagdahl and Holman, *J. Am. Chem. Soc.,* 72, 701 (1950).

2. Class One—Gradations of Eluents Based on Differences between Homologs

Because of convergence in homologous series the members near the beginning of the series show greater differences among themselves than higher members. The first few members, particularly the first member, may show exaggerated differences in properties. Rossini[5] pointed out that the introduction of a CH_2 group does not produce a constant increment in the heat of combustion of normal paraffins and primary alcohols until the number of carbon atoms exceeds five.

When they are compared against benzene as the adsorptive and silica gel as the adsorbent the alcohols fall in the series of increasing strength of adsorption:[6] isoamyl, *n*-butyl, *n*-propyl, ethyl, methyl (see Fig. III-6). The same order of strength of adsorption is observed against purified charcoal[6] (Fig. III-7), but the benzene is more strongly adsorbed than the alcohols. Further examples of eluent behaviors of homologs are contained in Table III-3. In general, the behavior as eluents will follow the homologous series; the direction, whether up or down the series, is considered below.

3. Class Two— Gradations of Eluents Based on Differences in Concentration

The effect of admixture on eluting power can be derived from the discussion in Chapter III. With water–alcohol mixtures the eluting effect increased with percent alcohol, markedly for acetic, tartaric, succinic, and oxalic acids, less so for benzoic and salicylic acids on charcoal (Fig. III-4). In general, it may be said that admixture improves eluting ability of a eluent. This follows from the observation of Heymann and Boye[7] that adsorption of a substance from a pure solvent is almost always lowered upon addition of a second solvent. This implies, also, *that a binary eluent will show a maximum eluting power at some concentration, and that this eluting power will be greater than that of either pure component.* (See below, Table V-4.) The effects of admixture with three or more components in the eluent seem not to have been worked out very thoroughly.

[5] Rossini, *J. Research Natl. Bur. Standards,* 13, 21, 189 (1934).

[6] Bartell and Scheffler, *J. Am. Chem. Soc.,* 53, 2507 (1931).

[7] Heymann and Boye, *Z. physik. Chem.,* A150, 219 (1930).

4. Class Three—Gradations of Eluents Based on Differences in Functionality

In this classification belong many of the series of eluents found in the literature. Trappe[8] set up such a series on the basis of heats of wetting and other properties. These relations are shown in Table IV-8. He named this the "eluotropic series." The gist of this series is repeated in Table V-1 for comparison with other series, and the order is reversed for convenience in application (see below). A somewhat different series is used

TABLE V-1

Trappe Eluotropic Series[8]

(Eluent power[a] increases down the table)

Petroleum ether
Cyclohexane
Carbon tetrachloride
Trichloroethylene
Toluene
Benzene
Dichlorethylene
Chloroform
Ether
Ethyl acetate
Acetone
n-Propyl alcohol
Ethyl alcohol
Methyl alcohol
Water

[a] Against polar solids (see below).

TABLE V-2

Graded series of eluents taken from the papers of Reichstein and coworkers

(Eluent power[a] increases down the table)

Petroleum ether
Benzene (anhydrous)
Ether (absolute)
Chloroform
Methanol
Ethyl acetate
(Glacial acetic acid)

[a] Against Brockmann alumina.

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[8] Trappe, *Biochem. Z.*, 305, 150 (1940).

by Reichstein for selective elution of mixtures from alumina columns.[9] A series derived from some of his work is shown in Table V-2. Essentially the same series is used by Ruzicka.[10] It is evident that these two series do not agree in detail. Strain[11] has given a table of eluents which is more extensive than the previous two (see Table V-3). It is recognized that all of these series are subject to some variation depending upon the type of adsorbent and the nature of the adsorbed compounds.

TABLE V-3

Strain Graded Series of Eluents[11]

(Eluent power[a] increases down the table)

Petroleum ether, b.p. 30–50°
Petroleum ether, b.p. 50–70°
Petroleum ether, b.p. 70–100°
Carbon tetrachloride
Cyclohexane
Carbon disulfide
Ether (anhydrous, alcohol-free)
Acetone (anhydrous, alcohol-free)
Benzene
Toluene
Esters of organic acids
1,2-Dichloroethane, chloroform, dichloromethane
Alcohols
Water (variations with changes in *p*H and salt concentration)
Pyridine
Organic acids
Mixtures of acids or bases with water, alcohol, or pyridine

[a] *Against polar solids (see below).*

5. Use of a Graded Series of Eluents

The value of a graded series of eluents is that if one member of the series succeeds in desorbing a portion of an adsorptive, then another, more powerful eluent, should bring off a further portion of adsorptive. An example of such an application is taken from a paper by Reichstein and von Euw[12] and is shown in Table V-4. A crude acetylated benzene

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[9] Neracher and Reichstein, *Helv. Chim. Acta,* 19, 1382 (1936); von Euw and Reichstein, *ibid.,* 31, 883 (1948); and numerous papers in the intervening years and since from this laboratory.

[10] Jeger, Bischof, and Ruzicka, *Helv. Chim. Acta,* 31, 1319 (1948); and numerous earlier papers from this laboratory.

[11] H. H. Strain, *Chromatographic Adsorption Analysis.* Interscience, New York, 1945, p. 66.

[12] Reichstein and von Euw, *Helv. Chim. Acta,* 24, 247E (1941).

TABLE V-4

Fractionation of an Extract[12]

Fraction No.	Solvent	Residue on evaporation
1	65% benzene + 35% petroleum ether	60 mg. syrup
2	80% " + 20% " "	
3	100% benzene	
4	" "	
5	" "	
6	" "	
7	99% benzene + 1% ether	
8	99% " + 1% "	
9	98% " + 2% "	23 mg. crude, from which 2.5 mg. leaflets, m.p. 184–185°
10	97% " + 3% "	
11	96% " + 4% "	
12	94% " + 6% "	
13	92% " + 8% "	19 mg. crude, from which 4 mg. needles, m.p. 213–215°
14	87% " + 13% "	
15	80% " + 20% "	44 mg. crude, from which 6 mg. T-diacetate, m.p. 209–211°
16	70% " + 30% "	
17	55% " + 45% "	100 mg. syrup
18	40% " + 60% "	
19	100% ether	
20	" "	
21	" "	
22	" "	23 mg. crude, from which 2 mg. crystals, m.p. 205–206°
23	99% ether + 1% acetone	
24	" " " "	
25	98% ether + 2% acetone	
26	" " " "	
27	97% " + 3% "	mixture
28	96% " + 4% "	
29	95% " + 5% "	
30	94% " + 6% "	40 mg. M-acetate
31	92% " + 8% "	
32	90% " + 10% "	
33	88% " + 12% "	
34	85% " + 15% "	mixture
35	80% " + 20% "	
36	75% " + 25% "	
37	70% " + 30% "	
38	60% " + 40% "	
39	50% " + 50% "	
40	40% " + 60% "	
41	49.5% ether +49.5% acetone +0.5% chloroform +0.5% methanol	
42	49% " +49% " +1% " +1% "	
43	48% " +48% " +2% " +2% "	
44	46% " +46% " +4% " +4% "	

extract prepared in the process of working up a steroid mixture weighed 1.21 g. and was applied to a column containing 40 g. alumina (Brockmann). The column was treated with the solvents named in Table V-4, about 120 cc. of each being used. The percolates were evaporated down and the residues weighed. A further brief description of the fractions as reported by Reichstein and von Euw is given below.

Fractions 1–8 yielded a syrup from which, besides a little free sulfur, no crystals could be separated. Fractions 9–12 on crystallization from petroleum ether and recrystallization from ether gave 2.5 mg. of colorless leaflets, m.p. 184–185°. These could not be identified. Fractions 13 and 14 were crystalline, m.p. 190–208°; recrystallization from acetone–ether gave 4 mg. of colorless, unidentified, irregular needles, m.p. 213–215°. Fractions 15 and 16 melted at 190–205°. Recrystallization from ether yielded 6 mg. colorless prisms, m.p. 209–211°, identified by mixed melting point as T-diacetate. Fractions 17–21 could not be crystallized. Fractions 22–26 gave small crystal masses, m.p. 185–200°. Two recrystallizations brought the melting point to 205–206°. Fractions 27–29 gave a mixture of needle masses (m.p. 190–210°) and leaflets (m.p. 201–213°) which could not be separated. Fractions 30–33 yielded on crystallization from acetone–ether *ca.* 40 mg. of M-acetate, m.p. 218–221°. The fractions 34–38 consisted of mixtures which were rechromatographed and separated into U-diacetate and some Fa-diacetate. The last fractions 39–44 gave only brown syrup.

The rationale of this fractionation is apparent. The eluents are used in a graded series, starting with the weakest (this is why the other tables have been arranged, starting with the weakest eluent). Concentration gradation has been used to obtain small steps of elution increase between the functional gradations. If any question may be raised about the process it is the possibly minor one, mentioned above, that admixture usually increases eluent power, so that in admixture it may not be necessary to go to 100% of the second (admixed) liquid. This may not apply here. In any case, some recognition has been made of this in that the admixed liquid is added in initially small but gradually increasing ratio.

IV. GRADED SERIES OF ADSORBENTS

1. General Remarks

Some guide is needed to the choice of an adsorbent. An aid in this choice, as in the choice of solvents (eluents and developers) is to have available graded series of adsorbents. Then, if an adsorbent is found to be too strong for a given separation application, a weaker one may be taken from the list. Adsorbents of different strengths may be obtained by graded deactivation of a very active adsorbent, or by activation of a weaker one. This gradation by activation is in a sense analogous to Class One and Two gradations of eluents: the differences are in a sense differences in degree. Another gradation is obtained by changing the functional type of the adsorbent, whether by changing the surface through the activation process (see Chapter VII) or by changing the nature of the adsorbent. The gradations under discussion here are gradations in selectivity of adsorption. They usually are accompanied by differences in adsorptive capacity. It is easy to see that different selectivities would be found with different kinds of adsorbents. But even with a single very active adsorbent, the surface is very inhomogeneous as regards adsorption sites (Chapter I). Variation in selectivity on deactivation can therefore be explained: the deactivating agent covers up sites of high adsorptive power which show one kind of selective behavior, and leaves uncovered less strongly adsorbing sites with a different selectivity. What is meant by selectivity here is ability to adsorb the different components of a mixture to different extents.

2. Class One—Gradations of Adsorbents Based on Differences in Activity

This subject is discussed to some extent in Chapter VII. Here only the series will be mentioned and the general principles. The general principle is that with an adsorbent such as silica or alumina, or other substance which has a strong affinity for water, it is possible to control the activity of the adsorbent by adjusting the water content of the surface. A very active adsorbent alumina can be deactivated by admitting water (or methanol or corresponding substances) to it. Brockmann and Schodder[13] set up five grades of activation which could be judged by the ability of each grade to hold and separate specified dyestuffs. Müller[14] used the heat of wetting with a developer liquid to judge the grade of activity of alumina deactivated by addition of water. Tiselius deactivated charcoal with a prewash of diluted developer solution.[15] Müller also deactivated a very active alumina by mixing in a weakly active grade. Activation of an inactive adsorbent belongs also to this class. As an example of this may be mentioned the activation of commercial reagent grade silicic acid by suitable prewashing[16] (see Chapter VII).

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[13] Brockmann and Schodder, *Ber.*, 74, 73 (1941).

[14] Müller, *Verhandl. Ver. schweiz. Physiol.*, 21, 29 (1942); *Helv. Chim. Acta*, 26, 1945 (1943).

[15] Tiselius, *The Svedberg 1884–1944*, Almqvist & Wiksells, Uppsala, 1944, p. 370.

3. Class Two—Gradations of Adsorbents Based on Differences in Functionality of the Surface

The activity and specificity of the surface can be changed by the activation process, especially with charcoal, upon which a great deal of work has been done. As an example, Bartell and Lloyd[17] were able, by high temperature activation, to produce an organophilic surface on purified charcoal. With low-temperature activation in a highly oxidizing atmosphere a surface was produced which the investigators said approached in adsorptive properties, the hydrophilic silica. The properties of the surface of amphoteric adsorbents (such as alumina) can be changed by prewashing. The functionality can also be changed by coating the adsorbent surface (Chapter VII).

Gradations in functionality can be obtained by the use of different adsorbents. Strain[18] has ranked adsorbents on the basis of increasing strength (Table V-5), with, of course, an awareness of the contingency

TABLE V-5

Strain Graded Series of Adsorbents[18]

(Strength of adsorption increases[a] down the table)

Sucrose, starch
Inulin
Magnesium citrate
Talc
Sodium carbonate
Potassium carbonate
Calcium carbonate
Calcium phosphate
Magnesium carbonate
Magnesia (Merck)
Lime (freshly and partially slaked)
Activated silicic acid
Activated magnesium silicates
Activated alumina, charcoal, magnesia (Micron brand)
Fuller's earth

[a] Depending on the solvent, at least.

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[16] Schroeder, *Ann. N. Y. Acad. Sci.,* **49,** 204 (1948).

[17] Bartell and Lloyd, *J. Am. Chem. Soc.,* **60,** 2120 (1938).

[18] H. H. Strain, *Chromatographic Adsorption Analysis.* Interscience, New York, 1945, p. 50.

of the relations. Sometimes a group of adsorbents may show similar selectivity. The choice of one of them then rests upon other considerations. For example, Lew, Wolfrom, and Goepp[19] report that in the separation of sugars and derivatives seven clay adsorbents which were tried showed about equal adsorptive selectivity based on an arbitrary requirement: the ability to separate a mixture of sorbitol and D-mannitol. One of these of intermediate adsorptive strength was chosen for standard use.

Excellent examples of differences in functionality of the surface are provided by exchange adsorbents (Chapter IX). Resins are available with only one type of exchanging group in the surface. It is then easy to rank such substances: among the cation exchangers, the carboxylic *vs.* sulfonic functional group resins; among the "acid adsorbers," the amine *vs.* quaternary ammonium resins.

V. ROLE OF THE INTERFACE

Certain properties of the interface at which the adsorption occurs play an important part in determining the extent of adsorption. This has been discussed by Bartell and Davis[20] in connection with liquid–liquid interfaces. They showed that the effectiveness of a given concentration of ethyl, *n*-propyl or *n*-butyl alcohols in lowering interfacial tension was greatest at the water–heptane interface, less at the water–benzene interface, and still less at the water–methyl *n*-amyl ketone interface. The interfacial tensions between the pure liquids are water–*n*-heptane 50.8_5; water–benzene 34.2_8; water–ketone 12.4_6 dynes/cm. It seemed that the greater the original interfacial tension the more marked the lowering of that tension at a given equilibrium concentration of the adsorptive in the water phase. Calculations, some of them of a semiquantitative nature, indicated that the extents of adsorption of the alcohols were proportional to the lowering of the interfacial tension produced. A greater lowering was possible at the water–heptane interface than at the water–ketone interface, and greater adsorption occurred, even at higher alcohol concentrations. The authors point out that the total amount of free surface energy at an interface is not the chief factor that determines the extent of adsorption, but rather the available free surface energy. The alcohols were adsorbed to approximately the same extent at a water–air surface and a water–heptane surface. The total free surface energies are about 72 and 51 ergs/cm.^{2}, but even when the water–air surface is completely covered with solute a free surface energy of some 22 ergs/cm.^{2} remains—that is, the available free surface energy is some 50 ergs/cm.^{2}. With the water–heptane interface it may be possible to increase the concentration of solute to the point where the phases become miscible and the interface disappears. In such a case all of the free interfacial energy would be available for adsorption. A corollary of this would seem to be that the more unalike (chemically, or in polar nature) two phases are that form an interface, the greater the extent of adsorption is likely to be at that interface for a given phase equilibrium concentration. The transfer of this concept to adsorption at solid–liquid interfaces is beset by difficulties.

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[19] Lew, Wolfrom, and Goepp, Jr., *J. Am. Chem. Soc.,* 68, 1449 (1946).

[20] Bartell and Davis, *J. Phys. Chem.,* 45, 1321 (1941).

VI. VALUE OF HEAT OF WETTING AS A GUIDE

As was pointed out above, Müller[21] used heat of wetting of an adsorbent by a developer to judge the activity of the adsorbent. The basis of this use is the belief that heat of wetting is a measure of extent of adsorption. Berl and Wachendorff[22] concluded that extent of adsorption (from water, toluene, or tetralin on charcoal or silica) of a given component will be less from a solvent with a higher heat of wetting of the adsorbent than from one with a lower heat of wetting, for the former will be more strongly adsorbed, and so compete more effectively for the surface. Grimm, Raudenbusch, and Wolff[23] came to a similar conclusion. This generalization was used by Trappe[24] in setting up the eluotropic series (Table IV-8). On the other hand, Bartell and Fu[25] showed, in a study of the heat of wetting of sugar charcoal by binary liquid mixtures, that α-bromonaphthalene shows a comparatively low heat of wetting of charcoal (25.1 cal./g. charcoal) but is strongly adsorbed from nitrobenzene, which shows a much higher heat of wetting (31.7 cal./g. charcoal). Bartell and Fu point out that the heat of wetting is a measure of the total surface energy change and not the free surface energy change. The latter, measured as adhesion tension, is about 89.2 for α-bromonaphthalene and lower, about 78.7 dynes/cm., for nitrobenzene. This is the reason why the α-bromonaphthalene is more strongly adsorbed. This shows that entire reliance cannot be placed on heat of wetting as a guide to the extent of adsorption of a liquid. However, it is nevertheless so that the generalization holds in most cases and therefore is useful. Tables V-6 (see also Tables

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[21] Müller, *Helv. Chim. Acta.*, 26, 1945 (1943).

[22] Berl and Wachendorff, *Kolloid-Z.*, 36, (Zsigmondy Festschrift), 36 (1925).

[23] Grimm, Raudenbusch, and Wolff, *Z. angew. Chem.*, 41, 104 (1928).

[24] Trappe, *Biochem. Z.*, 305, 150 (1940).

[25] Bartell and Fu, *J. Phys. Chem.*, 33, 1758 (1929).

III-8 and III-9) contain a collection of series of eluents based on data of this sort.

Bartell and Greager[26] used a simple test, the absorption of liquid by a powder, to obtain a relative measure of adhesion tension. Liquids with little adhesion for the solid particles do not wet them well, air is entrapped, and the powder does not adsorb much liquid. When the liquid shows a zero contact angle with the solid, if the adhesion tension is low, more liquid is adsorbed; but with zero contact angle and a high adhesion tension less liquid is adsorbed because the neighboring particles are drawn together.

TABLE V-6a

Order of Increasing Eluent Power (down the series) Judged from Various Data

Order[a] against TiO_2, SiO_2, SnO_2, ZrO_2, $ZrSiO_4$, $BaSO_4$, that is, polar solids[b]
Isooctane
Benzene
Carbon tetrachloride
Nitrobenzene
Butanol
Ethyl acetate
Butyric acid
Ethanol
Water

[a] Relative heats of immersion of the powders in the solvents—Boyd and Harkins, *J. Am. Chem. Soc.*, **64,** 1190 (1942); free energy change on immersion—Boyd and Livingston, *J. Am. Chem. Soc.*, **64,** 2383 (1942); energy of emersion—Harkins and Boyd, *J. Am. Chem. Soc.*, **64,** 1195 (1942).

[b] Not all liquids were tested against all solids, but of those tested the order was consistent with this.

TABLE V-6b

Order of Increasing Eluent Power (down the series) Judged from Various Data

Order against silica gel from relative heats of wetting[a]	Order against quartz from heats of wetting[b]	Order against silica from adhesion tension[c]
Hexane	Carbon disulfide	α-Bromonaphthalene
Carbon tetrachloride	Benzene, carbon tetrachloride	Benzene
Chloroform		Toluene
Ethylbenzene	Acetic acid	Chloroform
Chlorobenzene	Ethanol	Butyl acetate
Benzene	Water, methyl alcohol	Ethyl carbonate
Nitrobenzene		Isobutyl alcohol
Water		Water
Acetone		

[a] Bartell and Almy, *J. Phys. Chem.*, **36,** 985 (1932).

[b] Heymann and Boye, *Kolloid-Z.*, **63,** 154 (1933).

[c] Bartell and Greager, *Ind. Eng. Chem.*, 21, 1248 (1929).

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[26] Bartell and Greager, *Ind. Eng. Chem.*, 21, 1248 (1929).

TABLE V-6c

Order of Increasing Eluent Power (down the series) Judged from Various Data

Order against sugar charcoal from adhesion tension values[a]	Order against carbon black from adhesion tension values[b]	Order against charcoal from heat of wetting[c]
Water	Water	Water
Ethyl alcohol	Isobutyl alcohol	Ethyl alcohol
Ethyl carbonate	Ethyl carbonate	Carbon tetrachloride
Acetone	Butyl acetate	Benzene
Nitrobenzene	Decalin	Carbon disulfide
Benzene	Tetralin	Methyl alcohol
α-Bromonaphthalene	Benzene	
Carbon disulfide	Toluene	
	α-Bromonaphthalene	

[a] Bartell and Fu, *J. Phys. Chem.*, **33**, 1758 (1929). Bartell and Sloan, *J. Am. Chem. Soc.*, **51**, 1637 (1929).
[b] Bartell and Greager, *Ind. Eng. Chem.*, **21**, 1248 (1929).
[c] Heymann and Boye, *Kolloid-Z.*, **63**, 154 (1933).

VII. PREDICTION OF RELATIVE EXTENT OF ADSORPTION

1. General Remarks

The series of eluents and adsorbents presented so far in the tables are all more or less one-sided. They apply at most to two of the three materials (adsorbent, solvent, and adsorptive) involved in the adsorption. In order to deal with an actual problem all three may need to be considered. For this purpose the *relative* polarities of the three serve as a basis for choosing solvent and adsorbent.

2. Relative Polar Character

Relative polarity was discussed in the previous chapter. In general, polar character in a molecule implies an ability to interact with other molecules (of the same or different kind). The interactions are not specified. They include dispersion, orientation, induction, ion–dipole, hydrogen bonding, and other "physical" interactions and also even chemical interactions. The polar character increases with the intensity of the interaction; with the extent of departure, one might say, from "ideal" behavior. Since there is no easy way of giving a quantitative meaning to this term, the polar character of one molecular species is judged *relative* to that of another. This can be done on a "more or less" basis using chemical principles such as were discussed in Chapter IV.

On considering adsorbents, solvents, and adsorptives some useful rules may be derived, for not only are such important properties as *relative* solubility and *relative* wetting power predictable from *relative* polarity, but also the tables of elution series show some order, their contingent nature becomes more apparent, and they become more useful. It would appear, for example, that *generally the order of increasing extent of adsorption on silica is the reverse of that on sugar charcoal*. The more polar the molecule the more strongly is it adsorbed on polar silica, and the less polar, the more strongly adsorbed on nonpolar charcoal. A further generalization which holds fairly well is that other things being equal the order of adsorption on silica will hold for other polar solids, such as alumina, silicic acid, titanium oxide, calcium carbonate; and that the order of extent of adsorption to charcoal will hold also for other nonpolar (in adsorption behavior) solids, such as talc, stibnite, graphite, and paraffinlike solids (*e.g.*, some "plastics").

But remembering the definition of relative polar character it is not surprising to find variations from the rules. Some charcoals can show exceedingly polar surfaces (Chapter VII); molecules like benzene are more polarizable than others; acetone and similar carbonyl compounds show marked acceptor power in hydrogen bonding, while chloroform and carboxylic acids show donor ability. In a particular case, one of these properties may have an exaggerated effect on the adsorption, more than would be predicted from the rote application of rules. Thus the tables and rules guide without dictating. One balances the particular case against the general rule.

After balancing the relative polar characters of adsorbent, solvent, and adsorptive, the recognition of the competition for the limited surface of the adsorbent completes the list of the more important factors that enter the prediction. Again the emphasis is on *relative* behavior. There is only a limited area available to the solvent and adsorptive molecules. Geometrically speaking, it may be available equally to both molecules, but of course spatial factors may make more surface available to one than to another molecule. Barring extreme cases the distribution between bulk phase and interface will be governed by the relative polar characters of solvent and adsorptive *vis á vis* adsorbent.

VIII. GENERAL RULES FOR PREDICTING RELATIVE EXTENT OF ADSORPTION

With these considerations in mind, some useful rules may be presented to guide the prediction of relative extents of adsorption.

Rule 1. Greater adsorption to a surface will occur from that system which produces the greater lowering of interfacial tension. This rule follows from the

Gibbs relation. The interfacial tension is a manifestation (in part) of the unlikeness of the two phases. The adsorptive, as the result of adsorption, tends to reduce this unlikeness and to make the transition in properties at the interface less abrupt A corollary of this rule is that *a liquid which is highly adsorbed by a solid will show a low interfacial tension against the solid* (and a high adhesion tension, or spreading pressure).

Rule 2. The extent of adsorption is usually greater from solvents in which the adsorptive is less soluble. Lundelius[27] attempted to state this rule quantitatively. The phenomenon has been given explicit chromatographic application by Tiselius,[28] and by Holman and Hagdahl.[29] A corollary to this rule is that *for a given adsorptive the better solvent will make the better eluent.* This rule can be expected to hold well, particularly in those cases in which the solvents being compared show about the same interfacial tension toward the adsorbent being used.[30] The various rules by means of which solubility may be predicted, and the tests for determination of solubility are useful in conjunction with this rule.

Rule. 3. The more polar the substance the more extensive its adsorption at a polar surface, other things being equal. A corollary to this rule is that *a polar substance will be better adsorbed from a nonpolar solvent than from a polar one.*

Rule 4. The less polar a substance the more extensive its adsorption at a nonpolar surface, other things being equal. But the range of values observed is usually not as wide as that found with polar solids. This may be one reason why polar solids are more favored for adsorption separations (except special separations such as decolorization); they are available with a wider range of activity.

Rule 5. Extent of adsorption changes in a regular manner along an homologous series. This rule is implicit in the concept of homology. Taken with Rules 3 and 4 a corollary follows: *since relative polarity decreases up an homologous series, extent of adsorption to nonpolar surfaces should increase up the series.* This is a restatement of the Traube relation. Another corollary might be stated: *since relative polarity decreases up the homologous series, extent of adsorption to polar surfaces should increase down the series.* This is a restatement of the Holmes reversal of the Traube rule. Rule 2 would warn, however, that, since solubility usually decreases (with any solvent) with sufficiently great increase in molecular weight, this second corollary must be applied with discrimination.

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[27] Lundelius, *Kolloid-Z,* 26, 145 (1920).

[28] Tiselius, *Arkiv Kemi, Mineral. Geol.,* B26, No. 1 (1948).

[29] Holman and Hagdahl, *Arch. Biochem.,* 17, 301 (1948); *J. Biol. Chem.,* 182, 421 (1950).

[30] Bartell and Fu, *J. Phys. Chem.,* 33, 678 (1929).

CHAPTER VI

On the Nature of Separation Processes

I. INTRODUCTION

In this chapter there are classified and compared a number of separation processes. The chemical engineer with his concept of unit processes will find this classification to strike a familiar note; the chemist, who often looks at separation processes with a less practical orientation, may find this chapter suggestive. The objective is to set adsorption separations of all kinds in logical relation to each other and to place them in context, so to speak, among all the other related separation processes.

Separation processes may be divided, for our purposes, into two classes: those which utilize in the separation a distribution between two phases, and those which do not. The latter class which includes such processes as centrifugation, electrophoresis, electrolysis, electromagnetic separation, etc. will not be discussed. It is the purpose here to point out in a systematic yet general way the similarities in principle and the differences in application of a large number of those processes which utilize pairs of phases ("phase-pairs"). It will be quite impossible to discuss all possible phase-pair distributions here. Instead, cross-tables will be utilized together with examples of a few of the processes.

II. CROSS-TABLE OF DISTRIBUTION PROCESSES

In separating the components of a mixture by means of distribution, two phases are employed. The components of the mixture distribute themselves into the phases in ratios different from the ratio in the original mixture. The distribution having occurred, the phases can be separated mechanically, and the components in the new ratios recovered from each phase. The natures of the distributions will of necessity depend upon the kinds of phases used in the phase-pair. The various possibilities have been set forth in a cross-table (Table VI-1) together with *some* of the separation processes that rely on the particular distributions. (A few selected references are given for the various processes. The literature is too voluminous to be treated otherwise.) Surface phases have been introduced not only for reasons of formal symmetry but because in experience the

TABLE VI-1

Cross-Table of Possibilities for Separation Processes Involving Distribution into Two Phases, with Some Examples of Processes

Phases in contact	Gas or vapor (V)	Liquid (L)	Solid (S)
	BULK PHASES		
Gas or vapor (V)	V–V (atmolysis,[1] gas diffusion[2])		
Liquid (L)	V–L (distillation,[3] absorption[4])	L–L (solvent–solvent extraction[5])	
Solid (S)	V–S (sublimation[6])	L–S (crystallization[7])	S–S (enfleurage[8])
	SURFACE PHASES		
Mobile (surface of a liquid) (M)	V–M (foam separation,[9] flotation[10])	L–M (emulsion separation[11])	
Immobile (surface of a solid) (I)	V–I (gas adsorption[12] hypersorption[13])	L–I (adsorption from solution,[14] chromatography[15])	S–I (segregation in crystal masses)

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[1] E. Urbain and R. Urbain, *Compt. rend.*, **176**, 166 (1923).

[2] Hogerton, *Chem. & Met. Eng.*, **52**, Dec., 98 (1945). See also Barrer, *Trans. Faraday Soc.*, **35**, 644 (1939).

[3] W. A. Gruse and D. R. Stevens. *The Chemical Technology of Petroleum,* 2nd ed., McGraw-Hill, New York, 1942, p. 259 *et seq.* E. Kirschbaum, *Distillation and Rectification,* Chemical Pub. Co., New York, 1948. C. S. Robinson and E. R. Gilliland, *Elements of Fractional Distillation,* 3rd ed., McGraw-Hill, New York, 1939. *Distillation (Technique of Organic Chemistry,* Vol. IV), Weissberger, ed., Interscience, New York, 1950.

[4] T. K. Sherwood, *Absorption and Extraction,* McGraw-Hill, New York, 1937. See also Fenske Carlson, and Quiggle, *Ind. Eng. Chem.*, **39**, 1322 (1947).

[5] Hunter and Nash, *J. Soc. Chem. Ind.*, **51**, 285T (1932); *Ind. Eng. Chem.*, **27**, 836 (1935). E. Jantzen, *Das fractionierte Destillieren und das fractionierte Verteilen als Methoden zur Trennung von Stoff-gemischen,* Dechema-Monographie, No. 48, Vol. 5, Verlag Chemie, Berlin, 1932. L. C. Craig, and D. Craig, "Extraction and Distribution," in *Technique of Organic Chemistry,* Vol. III, Weissberger, ed., Interscience, New York, 1950, p. 171 ff. See also footnote 4.

[6] Wilke, *Chem. Ind.*, **1948**, 34; Flosdorf, *J. Chem. Ed.*, **22**, 470 (1945). Barrer, *Proc. Roy. Soc. London,* **A167**, 392, 406 (1938); *Trans. Faraday Soc.*, **40**, 374, 555 (1944). Barrer and Ibbitson, *ibid*, **40**, 194, 206 (1944).

[7] F. Quade, in J. Houben, ed., *Die Methoden der organischen Chemie,* Vol. I. 3rd ed., Thieme, Leipzig, 1925 (Edwards Bros., Ann Arbor 1943) p. 554 ff. E. H. Archibald, *The Preparation of Pure Inorganic Substances,* Wiley, New York, 1932. R. S. Tipson, "Crystallization and Recrystallization," in *Technique of Organic Chemistry,* Vol. III, Weissberger, ed., Interscience, New York. 1950, p. 363 ff.

[8] W. A. Poucher, *Perfumes, Cosmetics and Soaps,* Vol. II, 4th ed., Van Nostrand, New York, 1932, p. 40 ff.

[9] Schütz, *Trans. Faraday Soc.*, **42**, 437 (1946). Bader and Schütz, *ibid.*, **42**, 571 (1946). Shedlovsky, *Ann. N. Y. Acad. Sci.*, **49**, 279 (1948).

distributions employing surface phases are quite analogous to those employing bulk phases. All the adsorption processes fall in this group.

III. OPERATIONS INVOLVED IN THE PROCESSES

The actual separation process consists of certain definite operations which may be generalized to cover all of the distributions listed in Table VI-1.[16]

Operation 1. The mixture to be separated, dissolved in, or constituting one of the phases is by some means brought into contact with the other phase. Often, a rather specialized machine is used for this operation and the subsequent ones.

Operation 2. Contact between the phases of the phase-pair is maintained for a period to permit the components of the mixture to become distributed into the phases. This period may be that required to reach equilibrium, but its length is not necessarily governed by this end.

Operation 3. The phases are separated by some mechanical means.

Operation 4. The mixtures of substances, in new ratios of their components, are recovered from the phases separately by some suitable method.

The machines used for the different operations and with the different phase pairs are of an extraordinary variety, though certain uniformities can be observed among them. Thus, for obtaining contact in distillation, solvent extraction, and absorption systems, vertical tubes containing baffles of one kind or another, saddles, rings, or bubble-cap sections may be used; or stirring by ebullition or by mechanical means may aid the achievement of contact. The duration of contact can be controlled through the rate of throughput of the phases and by the use of reflux (though this is not the sole purpose of reflux). Among machines for the mechanical separation of the phases may be listed the condensers on distilling columns and the filters or centrifuges used in crystallization separations.

Each given phase-pair in Table VI-1 can be made the basis of separa-

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[10] G. H. Buchanan, in J. Alexander, *Colloid Chemistry,* Vol. III, Reinhold, New York, 1931, p. 225 ff. Hassialis, *Ann. N. Y. Acad. Sci.,* 46, 495 (1946).

[11] Elkes, Frazer, Schulman, and Stewart, *Proc. Roy. Soc., London,* A184, 102 (1945).

[12] C. L. Mantell, *Adsorption,* Mc-Graw-Hill, New York, 1945. E. Ledoux, *Vapor Adsorption,* Chemical Pub. Co., New York, 1945.

[13] Berg, *Trans. Am. Inst. Chem. Eng.,* 42, 665 (1946). Kehde, Fairfield, Frank, and Zahnstecher, *Chem. Eng. Progress,* 44, 575 (1948).

[14] W. A. Gruse and D. R. Stevens, footnote 3, p. 319 ff. W. A. Helbig, in J. Alexander, *Colloid Chemistry,* Vol. VI, Reinhold, New York, 1946, p. 814.

[15] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography,* Wiley, New York, 1943. H. H. Strain, *Chromatographic Adsorption Analysis,* Interscience, New York, 1945. T. I. Williams, *An Introduction to Chromatography,* Blackie, London, 1946.

[16] Cassidy, *J. Chem. Ed.,* 23, 427 (1946); *Ann. N. Y. Acad. Sci.* 49, 143 (1948).

tion processes that differ among themselves in the ways in which the operations are carried out. This leads to a great diversity in detail, while at the same time enlarging the armamentarium of the chemist with some very subtle separation processes. Here again there appear similarities in principle that can be used for correlation and classification.

In connection with *Operation 1* four arrangements for contacting the phase-pairs can be distinguished: batch-wise, cascade, differential countercurrent and cocurrent contacting. The batchwise method is, in principle, quite distinct from the differential countercurrent. The cascade application is a multiple-stage, or multiplied-batchwise, method which is analogous to a systematic batchwise fractionation such as may be carried out on the basis of a "diamond pattern"[17]; the differential countercurrent is the limit that might *in some cases* be approached by a cascade operation in which the stages are very numerous. Examples of these processes for a number of solvent-pair distributions are given in Table VI-2. The cocurrent method, in which the members of the phase-pair pass in the same direction,

TABLE VI-2

Examples of Methods of Operation by Which the Various Indicated Phase-Pairs Are Utilized in Separation Processes

Separation process	Distillation	Solvent–solvent extraction	Adsorption	Crystallization
Phase-pairs utilized	(V-L)	(L–L)	(L–I)	(L–S)
Batchwise	Distillation of a volatile substance from essentially nonvolatile solvent[3]	Simple liquid–liquid extraction[5]	Simple decolorization[14]	Simple crystallization[7]
Cascade (multistage)	Bubble-cap tower operation[3, 4]	Systematic repeated extraction[18]	Systematic repeated adsorption[20]	Systematic recrystallization[21]
Differential countercurrent	Packed tower operation[3, 4]	Packed tower extraction[19]	Chromatography[15]; hypersorption[13]	Countercurrent crystallization[22]

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[17] Bush and Densen, *Anal. Chem.*, **20**, 121 (1948) .

[18] Ravenscroft, *Ind. Eng. Chem.*, **28**, 851 (1936). Martin and Synge, *Biochem. J.*, **35**, 91 (1941). L. C. Craig, *J. Biol. Chem.*, **155**, 519 (1944). L. C. Craig, Golumbic, Mighton, and Titus, *ibid.*, **161**, 321 (1945). See also footnote 16.

[19] Martin and Synge, *Biochem. J.*, **35**, 1358 (1941). Scheibel, *Chem. Eng. Progress.* **44**, 681, 771 (1948).

[20] Sanders, *Ind. Eng. Chem.*, **20**, 791 (1928).

[21] Richards and Hall, *J. Am. Chem. Soc.*, **39**, 531 (1917). Dennis and Wyckoff, *ibid.*, **42**, 985 (1920).

[22] Orr, *Trans. Faraday Soc.*, **37**, 587 (1941). See also Jeremiassen, U. S. Patent 2,164,111; 2,164,112 (June 27, 1939).

is industrially important but will not be considered here. It seems to be essentially a batchwise process.

These different ways of contacting phase-pairs show, apart from their difference in appearance, a very fundamental difference in principle.[23] For a given quantity of the phases the batchwise is the least efficient and the differential countercurrent the most efficient, other things being equal.

The separation processes involving differences at the level of *Operation 2* are not quite as numerous at present as might be considered possible. For each different method of contacting there could be imagined processes which differ by using either equilibrium or nonequilibrium distributions. Some examples of these methods are collected in Table VI-3. It will be evident, also, that the procedure under each method of contacting may be varied in another way without changing the principle of the method. For example, the cascade method, as well as the differential countercurrent method, may be carried out either in a nonsteady state operation or in a steady state operation. In the former a given quantity of material is distributed, possibly to equilibrium, and then fractions are removed, more or less slowly, until the entire quantity of material has been exhausted or until a determined state of the separation has been reached. In the latter type of operation the mixture is fed into the system at the same rate at which fractions are drawn off, a steady state being achieved throughout the machine being used for the separation. This type of system is sometimes called an "open" system; it is characterized by a stable gradient of some kind between the point of ingress of the mixture to the machine and the points of egress of the fractions.[26] Because of this gradient the steady state is not an equilibrium state over-all, since the latter condition would require the intensities of all forms of energy to be uniform.

TABLE VI-3

Phase-pair	Process relying on virtual equilibrium	Nonequilibrium process
V–L	Fractional distillation under reflux[3,4]	Nonequilibrium evaporation[24]; molecular distillation[25]
L–I	Simple decolorization[14]	Probably most chromatographic processes[15]

A closer approach to equilibrium in cascade and differential countercurrent processes can be achieved through the device of reflux. The amount of a phase which is drawn off in the separation process is made less than the amount which is available. The excess is turned back into the system to serve as a counterflowing agent. This is an effective means of controlling the duration of contact of the phases, and is applied at both ends of the column; it also provides more extensive contact.

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[23] Ravenscroft, footnote 18; also footnote 15.

[24] Washburn, *J. Research Natl. Bur. Standards,* 2, 476 (1929). See also footnote 25.

[25] Hickman, *Ind. Eng. Chem.,* 29, 968 (1937); *Chem. Revs.,* 34, 51 (1944); *Am. Scientist,* 33, 219 (1945); *Ind. Eng. Chem.,* 39, 686 (1947).

[26] Bertalanffy, *Science,* 111, 23 (1950).

Differences in the mode of carrying out *Operations 3* and *4* are of no particular interest here, nor will those separation processes be discussed in which several different types of distribution are utilized simultaneously. These latter are covered here in principle, though not explicity.

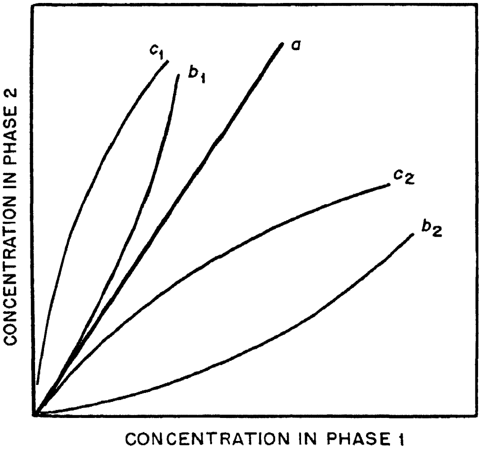

Fig. VI-1. Schematic diagram of the types of isotherms found in distribution between two phases.

Two questions may be raised at this point: why do the molecules of the mixture distribute themselves between the two phases in contact; and what factors control the relative amount of a given substance in each phase. The first of these questions has been attacked in many ways. The molecules of the mixture distribute themselves between the phases in a spontaneous process which is of itself irreversible. The tendency of the molecules to distribute themselves may be measured, as it occurs, as a rate. It may also be measured as a potential which will be greater the further removed the initial state of the system is from the equilibrium state. The escaping tendency of molecules from one phase into the other may be judged from the equilibrium distribution. It is sometimes measured in terms of fugacity.[27] The drive toward distribution of the components between the phases is sometimes explained as being due to the tendency to increase the entropy of the system. It is sometimes measured in terms of the probability of finding the molecule in one or the other phase. This was applied in the adsorption distribution by Langmuir.[28]

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[27] J. H. Hildebrand. *Solubility of Non-electrolytes*. 2nd ed., Reinhold, New York, 1936.

The chemical bases for explaining distributions are less general and often are particular to the mixture and phase-pair in question. They are often called upon to explain or aid in the prediction of distributions that depart from ideal behavior or to explain relative extents of distributions. Where the distributions occur between phase-pairs in which the concentration of the mixture to be separated is sufficiently low the ideal distribution behavior should be approached. Under such circumstances the ratio of concentrations of a component A, for example, in the two phases should be constant over a concentration range and at a given temperature.

The common observation is that at practical concentrations of A in most phase distributions the distribution ratio at a given temperature is not constant with the concentration. If the concentration of A in phase *1* is plotted against that in phase *2* an isotherm is obtained which, in the ideal case is a straight line (Fig. VI-1*a*). Departure from ideality may take the forms shown by the curves in Figures VI-1*b* and 1*c*.

Isotherms such as those shown in Figure VI-1 are found in many distributions. For example, for vapor–liquid distributions curve *a* represents a binary mixture that obeys Raoult's law. The *b* type of curve is given by mixtures that deviate in a negative manner from Raoult's law; positive deviation yields curves of type *c*[27]. Positive deviations are shown in mixtures in which the vapor pressures are greater than would be expected from Raoult's law. They may be expected of mixtures the constituents of which differ markedly in polarity, or one of the constituents of which associates in the liquid state. Negative deviations are likely to occur when the constituents of the system interact strongly. In such cases the vapor pressure above the liquid is less than the ideal. In all cases the isotherms approach straight lines at high dilution. (See Volume IV of this series.)

In liquid–liquid systems isotherms of the three types are found. The straight line (Fig. VI-1*a*) is approached at high dilution in all systems. In those systems in which the given solute has the same molecular weight in both solvents the straight-line function is likely to hold over a considerable range of concentrations; curves of types *b* and *c* are obtained as departures from the ideal behavior.[29] (See Volume III of this series.)

Similar isotherms have been encountered in the adsorption distribution. These have been discussed by a number of authors and some comparisons made between adsorption and other distributions.[30] Isotherms observed in vapor-immobile interface distributions have been described and explained by Brunauer[31] (see Fig. II-1), Cassel,[30] and Gyani.[32] In systems involving mobile interfaces, or involving solution-immobile interfaces the isotherms are usually of the type *c*.

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[28] Langmuir, *Colloid Symposium Monograph* 3, 48 (1925).

[29] Jantzen, footnote 5. Craig, footnote 5.

The rate of attaining equilibrium in a distribution is influenced by many factors, some of which aid and others of which hinder the distribution process. Among those which aid in the attainment of equilibrium the most important is intimacy of contact of the phases. It is evident that the rate of attaining equilibrium will be greater the shorter the average path which the molecules of *A* have to traverse within and between phases. For this reason the attainment of equilibrium in a given time of contact of the phases will be aided by intimacy of the contact. For L–L distributions the one liquid is dispersed into very small drops and stirred vigorously with the other; for V–L distributions the vapor is passed through the liquid in fine bubbles or is brought into contact with thin films of the liquid; for adsorptions the very finely divided adsorbent is stirred vigorously with the other phase or is used chromatographically (Chapter VIII).

Certain practical limits set themselves to the provision of intimate contact between the phases. If the droplets of liquid are made too small, then sometimes difficultly resolvable emulsions result, and the mechanical separation of the phases is hindered. Similarly, if the adsorbent is divided too finely it may become suspended or dispersed in the other phase and thus become difficult to separate.

The attainment of equilibrium may, in general, be aided by increase in temperature, since the rates of molecular motions are increased. However, the use of increased temperature may be undesirable on two counts. The equilibrium—attained faster in this way—may be less favorable to a separation, since the fine differences in the behavior of two components *A* and *B*, which may be produced by weak interactions of one kind or another, may tend to be ironed out by the increased kinetic energy. Also, since in some cases solubility is increased by rise in temperature the two phases in such cases may become sufficiently more soluble in each other that not only are differences in distribution of *A* and *B* between them affected adversely for the separation, but also they may become less easy to separate cleanly. Also, chemical interactions may develop.

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[30] Weigner, Magasanik, and Virtanen, *Kolloid-Z.*, **28**, 51 (1921). Frumkin. *Z. physik. Chem.*, **116**, 501 (1925). Angelescu and Comanescu, *Kolloid-Z.*, **44**, 288 (1928). Cassel and Formstecher, *ibid.*, **61**, 18 (1932). Cassel, *J. Phys. Chem.*, **48**, 195 (1944). Wohler and Wenzel, *ibid.*, **53**, 273 (1930). Heymann and Boye, *Kolloid-Z.*, **63**, 154 (1933). Broda and Mark, *Z. physik. Chem.*, **A180**, 392 (1937).

[31] S. Brunauer, *The Adsorption of Gases and Vapors*, Vol. I, *Physical Adsorption*. Princeton Univ. Press, Princeton. 1943.

[32] Gyani, *J. Phys. Chem.*, **49**, 442 (1945).

An important factor that hinders the attainment of equilibrium in many separations is the interfacial barrier that must be surmounted during the distribution. This barrier is the relatively stationary fluid film at the interfacial boundary between the two phases, through which passage of solute occurs by diffusion.[33] The barrier represented by this film has received considerable study in connection with absorption and distillation processes. L. C. Craig[34] has postulated that this barrier plays an important role in the difference between the bulk phase distributions and those involving interfacial phases. Wohler and Wenzel[35] have suggested that new polar forces due to the deformation of the adsorbed molecules on a solid surface may be responsible in part for the difference between adsorption and liquid–liquid partition.

Another complicating factor has already been mentioned. In an ideal distribution process the ratio of the concentrations of a given molecular species in the two phases would be constant.[36] However, in most actual cases this constancy is not observed. The departure from the ideal behavior is especially great in concentrated solutions, so that it becomes rather complicated to deal quantitatively with these separation processes.

In dealing with actual distributions two types of approach are taken to this problem. In the laboratory it is often possible to work with such dilute solutions that ideal behavior is approached. This makes the calculation of such systems much simpler. This approach is exemplified in the work of Martin and Synge,[37] Tiselius,[38] and L. C. Craig.[34] The other approach, which appears to be the only feasible one at present for dealing with separations of concentrated solutions (*i.e.*, most industrial and some laboratory separations), makes use of indices, factors, simplifying assumptions, and other adjustable parameters through which a manageable theory can be fitted to the experimental observations.[39]

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[33] Hunter and Nash, *J. Soc. Chem. Ind.*, **51**, 285T (1932); also Sherwood, footnote 4.

[34] L. C. Craig and D. Craig, "Extraction and Distribution," in *Technique of Organic Chemistry,* Vol. III, Weissberger, ed., Interscience, New York, 1950, p. 171 ff.

[35] Wohler and Wenzel, *Kolloid-Z.*, **53**, 273 (1930).

[36] Nernst, *Z. physik. Chem.*, **8**, 110 (1891). A. E. Hill, "Heterogeneous Equilibrium," in Taylor, *A Treatise on Physical Chemistry*, Vol. I, 2nd ed., Van Nostrand, New York, 1930, p. 467.

[37] Martin and Synge, *Biochem. J.*, **35**, 91, 1358 (1941). Consden, Gordon, and Martin, *ibid.*, **38**, 224 (1944).

[38] A. Tiselius, in E. O. Kraemer, ed., *Advances in Colloid Science*, Vol. I, Interscience, New York, 1942, p. 81. See also Claesson, *Arkiv. Kemi, Mineral. Geol.*, **A23**, No. 1 (1946).

[39] Randall and Longtin, *Ind. Eng. Chem.*, **30**, 1063 (1938). Thiele, *ibid.*, **38**, 646 (1946). Benedict, *Chem. Eng. Progress*, **43**, 41 (1947).

A further complication in separations is provided by the existence of constant distribution mixtures. In crystallization these may be eutectics,[40] or weakly bound complexes which are not separated under the conditions of most crystallizations (*e.g.*, low temperature). The analog in distillation is the existence of azeotropes.[41] These may be broken in a variety of ways.[42] In adsorption the analog is found in the mixtures which are adsorbed in the same ratio as they exist in the bulk phase.[43] It may be imagined that these can be separated by nonequilibrium chromatography (as azeotropes may be separated by nonequilibrium distillation).[41,42]

It is evident from this analysis that all these distribution processes are analogous in principle. In practice they differ with the nature of the phase-pair, which governs the kind of machine used in carrying out the separation, and with the manner of contacting the phase-pairs. They differ also in many details of operation which are discussed under the individual processes in other volumes of this series.

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[40] R. S. Tipson, "Crystallization and Recrystallization," in *Technique of Organic Chemistry,* Vol. III, Weissberger, ed., Interscience, New York. 1950, p. 363 ff.

[41] Washburn, *J. Research Natl. Bur. Standards,* 2, 476 (1929).

[42] Sunier and Rosenblum, *Ind. Eng. Chem., Anal. Ed.,* 2, 109 (1930).

[43] Williams, *Medd. Vetenskapsakad. Nobelinst.,* 2, No. 27 (1913). Wo. Ostwald and Izaguirre, *Kolloid-Z.,* 30, 279 (1922). Bartell and Sloan, *J. Am. Chem. Soc.* 51, 1643 (1929).

CHAPTER VII

Batchwise Adsorption and Decolorization. Lists of Adsorbents

I. INTRODUCTION

The practical application of adsorbents is an old art.[1,2] One of the most common uses of adsorption is for purification of gases or liquids. In such applications the objective often is to remove moisture, "color," "odor," or, in general, undesirable components of the mixture without affecting appreciably the desirable components. In another type of application, which may also be called purification, the object is to collect and concentrate one or more components of the mixture, leaving behind the others. These two uses may be combined: one fraction of the mixture is left in the purified solution; the other is recovered as an adsorbate.

A number of aspects of adsorbents and their use will be omitted here. There will be no discussion of methods of manufacture of adsorbents[3,4] or of special industrial applications, though some will be listed. There will be no discussion of the application of adsorbents in such uses as air conditioning,[4] dehydration,[4] gas masks,[4] solvent recovery,[4] petroleum refining,[5] sugar manufacture,[1,6] water purification,[7] catalysts, as carriers of insecticides or other agents, in medicinal applications, or in connection with adhesives, binding agents, etc.

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[1] V. R. Deitz, *Bibliography of Solid Adsorbents*. Washington, D. C., 1944; (obtainable from J. M. Brown, Revere Sugar Refinery, Charlestown, Mass.).

[2] J. W. McBain, *The Sorption of Gases and Vapours by Solids*. Routledge, London, 1932.

[3] O. Kausch, *Die aktive Kohle, Ihre Herstellung und Verwendung*, Knapp, Halle, 1932. F. Krzil, "Aktive Tonerde, Ihre Herstellung und Anwendung," in *Sammlung chemischer und chemisch-technicher Vorträge, Neue Folge*, Heft 41, Enke, Stuttgart, 1938; *Chem. Abstracts*, 26, 2017 (1932). C. L. Mantell, *Adsorption*, McGraw-Hill, New York, 1945. H. B. Weiser, *The Hydrous Oxides*, McGraw-Hill, New York, 1926.

[4] E. Ledoux, *Vapor Adsorption. Industrial Applications and Competing Processes*, Chemical Pub. Co., Brooklyn, 1945; also Mantell, *op. cit.*

[5] W. A. Gruse and D. R. Stevens, *The Chemical Technology of Petroleum*. McGraw-Hill, New York, 1942, p. 319 ff.

[6] J. W. Hassler, *Active Carbon, The Modern Purifier*. Industrial Chemical Sales Division, West Virginia Pulp and Paper Co., New York, 1941.

[7] J. R. Baylis, *Elimination of Taste and Odor in Water*. McGraw-Hill, New York, 1935.

TABLE VII-1

Surface Area and Density of Some Solid Adsorbents†

Material	Surface area		Bulk density, g./ml.	Reference
	M^2/g.	Gas (°C.)		
Carbonaceous Adsorbents				
Bone char, new	120	N_2 (−195°)	0.8	*d,p*
Coconut-shell charcoal	1700			*d*
Darco G-60	1300			*d*
Darco S-51	500			*d*
Granular Darco	620			
Darco carbon	560		0.36	
Columbia carbon	1397		0.42	*a*
Graphite, powdered	30.73			*b,p*
Carbon blacks (see also *z*):				
Arrow black (0.03 μ)	112			*b,d*
Acetylene black (0.05μ)	64.5			*b*
Micronex (0.03μ)	106.7			*b*
Thermatomic carbon (0.5μ)	6.81			*b*
Norit	930			*d,p*
Suchar	850			*d*
Petroleum coke	0.52			*d*
Zeo-Karb	0.2			*p*
Inorganic Adsorbents				
Activated alumina, Alorco	200	N_2 (−195°)	—	*f*
Activated clay -6	147	"	0.81	*a*
Activated clay -7	223	"	0.68	*a*
Activated alumina desiccant	175	"	0.81	*a*
Alumina, synthetic, 10–30 mesh	170	"	0.88	*s*
Asbestine pigment	4.1	H_2O (25°)	—	*c*
Attapulgus clay	170	N_2 (−195°)	—	*p*
Asbestos	18	"	—	*q*
Basic carbonate white lead	1.1	H_2O (25°)	—	*c*
Barytes pigment	0.59			*c*
Barium sulfate	0.43			*w*
Bauxite, 8–14 mesh	228	N_2 (−195°)	0.88	*a*
Arkansas I, 10–20 mesh	289		0.90	*r*
" II, " "	353		0.90	*r*
British Guiana, 10–20 mesh	280		0.90	*r*
French, 10–20 mesh	82.5		1.30	*r*
Arkansas 1, 10–30 mesh	236		0.97	
" 2 " "	176		0.93	
" 3 " "	200		0.86	
South America, flaky, 10–30 mesh	187		0.96	
Blanc fixe pigment	2.2	H_2O (25°)		*c*
Bentonite (<0.3μ)	18.7	N_2 (−195°)		*u*

Table continued

TABLE VII-1 (*continued*)

Material	Surface area		Bulk density, g./ml.	Ref.
	M^2/g.	Gas (°C.)		
Inorganic Adsorbents (*continued*)				
Brucine montmorillonite	12.3	"	—	*v*
Clay	10	"	—	*q*
Copper sulfate, anhydrous	6.23	"	—	*i*
Chromium oxide gel	228	"	—	*i*
Sintered	28.3	"	—	*i*
Diaspore, AlO(OH)	3.9	"	—	*v*
Diatomaceous earth	4.2	"	0.32	*a*
Diatomaceous earth	<1	"	0.29	*a*
Ferric oxide gel	211	C_2H_5OH	—	*h*
Water aged	52	"	—	*h*
Fuller's earth	129	N_2 (−195°)	0.55	*a*
Gibbsite, $Al(OH)_3$	0.31	"	—	*v*
Glass, spheres, 12μ	0.216	"	—	*x*
Sized beads (7.2μ)	0.55	"	—	*w*
Fritted, 8–14 mesh	0.69	"	0.87	*a*
Porous (Corning Glass)	120	"	—	*g*
Glaucosil	82	"	—	*i*
Halloysite	43.2	"	—	*v*
Illite (hydrous mica, <0.3μ)	97.1	"	—	*v*
Kaolinite (<0.3μ)	15.5	"	—	*v*
Kieselguhr	22.2	"	—	*j*
Lithopone pigment	2.3	H_2O (25°)	—	*c*
Montmorillonite	15.5	N_2 (−195°)	—	*v*
Montmorillonite	11.2	"	—	*u*
Palladium catalyst	0.35	"	—	*m*
Paper, insulating	0.55	"	—	*y*
Paris white	2	"	—	*q*
Porcelain, Coors	1.6	"	1.00	*a*
Potassium chloride (<200 mesh)	0.24	"	—	*i*
Pumice	0.38	"	—	*i*
Quartz, 400 mesh	0.361	"	—	*x*
Flint, 4–6 mesh	<1	"	1.53	*a*
Silica gel	620	"	—	*e*
Silica gel	765	"	—	*e*
Silica gel I, nonelectrolyzed	584	"	—	*i*
Silica gel II, electrolyzed	614	"	—	*i*
Silica gel	866	"	—	*k*
Silica gel	414	N_2 (−195°)	—	*t*
+5.2% Al_2O_3	541	"	—	*t*
Silica gel, 4–8 mesh	669	"	0.77	*a*
Silica gel, 10–30 mesh	602	"	0.78	*s*
Silica aerogel V	410	CCl_4	—	*l*

Table continued

TABLE VII-1 (*concluded*)

Material	Surface area		Bulk density, g./ml.	Reference
	$M^2/g.$	Gas (°C)		
		Inorganic Adsorbents (*continued*)		
Silica aerogel V	370	C_6H_6	—	*l*
Silica aerogel III	330	H_2O	0.92	*l*
Silica aerogel	393	Butane, (0°)	—	*h*
Silica aerogel	690	N_2 (−183°)	—	*h*
Silica aerogel, water aged	186	Butane (0°)	—	*h*
Silica-alumina gel, 4–8 mesh	280	N_2 (−195°)	1.00	*a*
Silica-alumina gel "	404	"	0.75	*a*
Silica-alumina gel "	467	"	0.69	*a*
Silica-alumina gel "	372	"	0.64	*a*
Silica-alumina gel "	409	"	0.55	*a*
Silica-alumina gel "	323	"	0.55	*a*
Silica-alumina gel "	201	"	0.68	*a*
Titanium dioxide pigment	8.2	H_2O (25°)	—	*c*
Titanium dioxide	13.9	N_2 (−195°)	—	*o*
Titanium dioxide	13.8	H_2O (25°)	—	*o*
Ultramarine blue pigment	13	"	—	*c*
Vermiculite*	0.52	N_2 (−195°)	—	*n*
Vermiculite, exfoliated*	10.35	"	—	*n*
Whiting pigment	2.6	H_2O (25°)	—	*c*
Zinc oxide pigment	2.4	"	—	*c*
Zinc oxide pigment K-1602	3.80	N_2 (−195°)	—	*w*
Zinc oxide pigment F-1601	9.48	"	—	*w*
Zinc oxide pigment G-1603	3.88	"	—	*w*
Zinc oxide pigment KH-1604	0.658	"	—	*w*
Zirconium orthosilicate	2.76	"	—	*w*

† Table VII-1, except for the values marked with an asterisk (*), is from Deitz, *Ann. N. Y. Acad. Sci.*, **49**, 315 (1948), Table 2, pp. 319–321.

[a] Drake and Ritter, *Ind. Eng. Chem., Anal. Ed.*, **17**, 787 (1945). [b] Emmett and De Witt, *ibid.*, **13**, 28 (1941). [c] D. Smith and Green, *ibid.*, **14**, 382 (1942). [d] Deitz and Gleysteen, *J. Research Natl. Bur. Standards*, **29**, 191 (1942). [e] Gleysteen and Deitz, *ibid.*, **35**, 285 (1945). [f] Krieger, *J. Am. Chem. Soc.*, **63**, 2712 (1941). [g] Emmett and De Witt, *ibid.*, **65**, 1253 (1943). [h] Harvey, *ibid.*, **65**, 2343 (1943). [i] Brunauer and Emmett, *ibid.*, **59**, 2682 (1937). [j] Anderson, *ibid.*, **68**, 686 (1946). [k] Joyner, Weinberger, and Montgomery, *ibid.*, **67**, 2182 (1945). [l] Kistler, Fischer, and Freeman, *ibid.*, **65**, 1909 (1943). [m] Emmett and Skau, *ibid.*, **65**, 1029 (1943). [n] Harris, *ibid.*, **71**, 363 (1949). [o] Jura and Harkins, *ibid.*, **66**, 1356 (1944). [p] National Bureau of Standards, *unpublished.* [q] Bugge, Kerlogue, and Westwick, *Nature*, **158**, 28 (1946). [r] La Lande, Jr., McCarter, and Sanborn, *Ind. Eng. Chem.*, **36**, 99 (1944). [s] Heinemann, Krieger, and McCarter, *ibid.*, **38**, 839 (1946). [t] Elkin, Schull and Roess, *ibid.*, **37**, 327 (1945). [u] Makower, Shaw, and Alexander, *Soil Sci. Soc. Am., Proc.*, **2**, 101 (1937). [v] Nelson and Hendricks, *Soil Sci.*, **56**, 285 (1943). [w] Emmett, "Symposium on New Methods for Particle Size Determination in the Subsieve Range," *A. S. T. M.*, **41**, 95 (1941). [x] Gaudin and Bowdish, *Mining Technol., A. I. M. M. E.*, **8**, No. 1666 (1944). [y] Stamm and Millett, *J. Phys. Chem.*, **45**, 43 (1941). [z] Smith, W. R., Thornhill, and Bray, *Ind. Eng. Chem.*, **33**, 1303 (1941).

II. BATCHWISE ADSORPTION

1. Requirement of Contact

A large surface area can be provided by using a finely divided adsorbent. It can also be obtained by using a very porous substance. Quite large surface areas are shown by substances which are both very porous and finely divided.[8] Table VII-1 shows the surface areas of a number of adsorbents. But from the discussion in the previous chapters it must be concluded that a "large surface area" is not the sole requirement for a useful adsorbent. There is needed a large surface area *accessible* to the adsorptive in question as well as a preferential ability to take up the adsorptive. These requirements are important in the evaluation of adsorbents.

2. Duration of Contact

It is essential not only to obtain contact between the mobile phase and the adsorbent surface, but also to permit sufficient duration of contact. The requirement of contact thus has two aspects: good contact, which provides that molecules of adsorptive need diffuse over only a short path to reach a surface; and duration of contact, which allows time for the adsorption reaction itself. These two aspects are usually not distinguished. Swearingen and Dickinson[9] studied the rates of adsorption of mono-, di-, and trichloroacetic acids by silica gel and blood charcoal. The rates of adsorption and the time required for reaching equilibrium were found to depend on the amount of agitation, the nature of the adsorptive, the concentration of the adsorptive, and the nature of the adsorbent. Kimball[10] has compared expressions for rates of adsorption (and desorption) with those for homogeneous reactions, and Roginskii[11] has discussed the movement and redistribution of molecules on a surface.

Maximum adsorption occurs at the equilibrium point, but this may not be a useful goal for any or all of several reasons. It may be impractical to wait for equilibrium in those cases where this state is approached slowly. For example, in the exchange adsorption of cupric ion from aqueous solutions on 20–30 mesh carbonaceous zeolite (Zeo-Karb-H) it was found by Beaton and Furnas[12] that most of the exchange had occurred in 6 to 8 hrs. 1.8 milliequivalents were taken up per gram of zeolite in 6 hrs. But adsorption continued slowly, so that at the end of 7 days the adsorption had increased to 1.9 milliequivalents per gram. This may be an example of a problem in contact,[13] the internal surface of the exchanger being somewhat less accessible to the ion than the outer surface of the particles.

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[8] Deitz and Gleysteen, *J. Research Natl. Bur. Standards,* 29, 191 (1942). Deitz, *Ann. N. Y. Acad. Sci.,* 49, 315 (1948).

[9] Swearingen and Dickinson, *J. Phys. Chem.,* 36, 534 (1932).

[10] Kimball, *J. Chem. Phys.,* 6, 447 (1938).

[11] Roginskii, *Acta Physicochim. U. R. S. S.,* 20, 227 (1945); *Chem. Abstracts,* 40, 11 (1946).

[12] Beaton and Furnas, *Ind. Eng. Chem.,* 33, 1500 (1941).

Again, the attainment of equilibrium may be undesirable in cases where substances to be separated show markedly different rates of adsorption. This situation has been mentioned in Chapter VI; it may be of importance to chromatography. Dubinin[14] noticed, when using fine-pored charcoal, that the appearance of reversal of the adsorption series with the acids propionic, valeric, and heptylic was increased when experiments were carried out using durations of contact insufficient for reaching equilibrium.

3. Recognition of Adsorption

The recognition that adsorption has occurred is generally an analytical problem. For convenience in surveying the possibilities in the face of a problem a number of methods are gathered in Table VII-2. The problem is important to chromatography and is treated further in Chapter VIII under the discussion of the recognition of zones.

4. Some Applications of Adsorbents

Adsorbents are used not only for removing molecularly dispersed substances from solution, but they are also used for removing colloidally dispersed substances,[15] as well as suspended matter of even larger particle size. Soaps may be adsorbed from suspension by some charcoals. Use of this is made in the removal of free acids from edible oils. The free acid is neutralized with alkali and the soap is adsorbed. This allows complete removal of the acid which otherwise, due to hydrolysis, would be distributed between the oil and caustic phases.[15]

It appears that some of these applications rest upon the fact that many adsorbents in aqueous or other ionizing solutions take on a characteristic charge (Table VII-3). Where this charge is opposite to that of the colloidal micelles or other particles, the adsorbent can effectively bring about flocculation and removal of these substances. The field does not seem to have been reported very thoroughly. Hassler[15] states that

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[13] Baum and Broda, *Trans. Faraday Soc.*, 34, 797 (1938).

[14] Dubinin, *Z. physik. Chem.*, 155, 116 (1931).

[15] J. W. Hassler, *Active Carbon, The Modern Purifier*, Industrial Chemical Sales Division, West Virginia Pulp and Paper Co., New York, 1941; *Ind. Eng. Chem*,. 32, 640 (1940).

TABLE VII-2. Examples of Ways in Which Adsorption May Be Followed

Physical methods[a,k]
- Measurement of weight change
- Optical measurements
  - Infrared (reflection in the near infra-red)[b]
  - Visible color[c–e]
  - Ultraviolet[e]
  - Fluorescence[e]
  - Index of refraction[f]
  - Optical rotation[e]
  - Turbidity[c,g]
- Measurements of P, V, and T[a]
- Electrometric titrations[h]
  - Conductivity
  - Neutralization
  - Oxidation-reduction
  - Precipitation
  - Polarography
  - Changes in dielectric properties
- Magnetic susceptibility

Chemical methods[h,k]
- Titrations with indicators
  - Neutralization
  - Oxidation-reduction
  - Precipitation
- Color reactions followed by physical measurements
- Gasometric reactions[i]

Physiological methods
- Color[j]
- Odor[j]
- Taste[j]
- Physiological activity of various kinds, such as Hormone action, Vitamin action, etc.

[a] See Chapter II. [b] Déribéré, *Compt. rend.*, **213**, 379 (1941); *Chem. Abstracts*, **36**, 6857.^{3} [c] F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. I, 3rd Ed., Van Nostrand, New York, 1948. [d] J. H. Yoe, *Photometric Chemical Analysis*, Vol. I, *Colorimetry*, Wiley, New York, 1928. [e] T. R. P. Gibb, Jr., *Optical Methods of Chemical Analysis*, McGraw-Hill, New York, 1942. [f] Bartell and Sloan, *J. Am. Chem. Soc.*, **51**, 1637 (1929); Claesson, *Arkiv Kemi, Mineral. Geol.*, **A23**, No. 1 (1946). [g] J. H. Yoe and H. Kleinmann, *Photometric Chemical Analysis*, Vol. II, *Nephelometry*, Wiley, New York, 1929. [h] I. M. Kolthoff and H. A. Laitinen, *pH and Electro Titrations*, 2nd ed., Wiley, New York, 1941; I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II, *Ttration Methods*, Interscience, New York, 1947. [i] Van Slyke, *J. Biol. Chem.*, **83**, 425 (1929); Van Slyke, Dillon, MacFadyen and Hamilton, *ibid.*, **141**, 627 (1941). [j] J. W. Hassler, *Active Carbon, The Modern Purifier*, Industrial Chemical Sales Division, West Virginia Pulp and Paper Co., New York, 1941. [k] A Weissberger, ed., *Physical Methods of Organic Chemistry*, 2nd ed., Part I, p. 897 ff.; Part II, pp. 1141 ff., 1241 ff., 1399 ff., 1651 ff., 1713 ff., 1785 ff., 1885 ff.

TABLE VII-3

Characteristic Charges Taken on by Some Particles in Water Suspension

Particles usually negatively charged	Particles usually positively charged
Clays: bentonites, montmorillonites	Alumina, basic hydroxides
Insoluble acids: tungstic, stannic	Sols of metal oxides, ferric oxide
Acid dyestuffs	Basic dyestuffs
Soap micelles	Invert soaps, "onium" soaps
Silica, glass	
Sols of metals, metallic sulfides	
Proteins in basic solution	Proteins in acid solution
Most charcoals[a]	
Cotton Paper Mastic	

[a] Purified sugar charcoal activated near 1000 °C. gave both positively and negatively charged particles; when activated at temperatures near 400°, or in a highly oxidizing atmosphere below 150° it gave only negatively charged particles (Bartell and Lloyd, *J. Am. Chem. Soc.*, **60**, 2120, 1938). For bibliography, see V. R. Deitz, *Bibliography of Solid Adsorbents*, obtainable from J. M. Brown, Revere Sugar Refinery, Charlestown, Mass. (1944).

whereas lyophobic colloids such as gold sols are removed by activated charcoal the effect appears to be due to salts in the adsorbent because an ash-free charcoal is without effect. This may be, however, a matter of the charge on the different charcoals. He states further that lyophilic colloids such as gelatin and gums are well adsorbed by some charcoals. Some chars (charcoals) when suspended in water act as negatively charged lyophobic substances in that they can be coagulated by cations, especially if the cations are strongly adsorbed.

Mantell[16] states that the majority of colored materials encountered in industry are negatively charged, and that ordinarily charcoals will decolorize such substances more efficiently the higher the acidity of the solution; oppositely charged substances, then, would be best adsorbed in alkaline solution, and amphoteric substances close to their isoelectric points. The adsorption of uncharged materials is less affected by acidity or alkalinity. The problems are, however, rather complex, so that it is difficult to lay down very general rules.

There is a large literature on the ability of adsorbents to adsorb ions.[17] Thus, charcoals can be produced which are negatively or positively charged in aqueous suspension or not charged at all. Alumina can be prepared by suitable washing treatments to act as anion or as a cation exchanger.[18] For example, if alumina is treated with acid it takes on anion-exchange properties; if the acid was HCl the adsorbent becomes capable of exchanging Cl^- ions for others[19] (see below).

The ability of adsorbents to take up charged particles sometimes becomes an inconvenience. Under some conditions the adsorbent, especially if it is finely divided, becomes peptized and is then difficult to remove from suspension. This is sometimes noticed with decolorizing charcoal, often in alcohol solutions. The charcoal becomes so well peptized that it passes through filter paper and even resists centrifugation. The remedy in this case is to stir into the suspension a small amount of filter paper pulp. This rapidly collects the charcoal particles, and the whole mass can then be filtered off. In other cases a finely divided powder of opposite charge, or a polyvalent ion, is stirred into the suspension until the particles are flocculated. An alternative procedure is to carry out the adsorption process (or decolorization) chromatographically.

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[16] C. L. Mantell, *Adsorption*. McGraw-Hill, New York, 1945.

[17] H. Freundlich, *Colloid and Capillary Chemistry*, 3rd ed., Methuen, London, 1926. Miller, *J. Phys. Chem.*, **30**, 1162 (1926). Dubinin, *Z. physik. Chem.*, **150**, 145 (1930). Roychoudhury, *J. Indian Chem. Soc.*, **8**, 433 (1931). Bartell and Lloyd, *J. Am. Chem. Soc.*, **60**, 2120 (1938).

[18] Schwab and Jockers, *Naturwissenschaften*, **25**, 44 (1937); *Angew. Chem.*, **50**, 546 (1937). Schwab and Dattler, *ibid.*, **50**, 691 (1937). F. Krczil, "Aktive Tonerde, Ihre Herstellung und Anwendung," in *Sammlung chemischer und chemisch-technischer Vorträge, Neue Folge*, Heft 41, Enke, Stuttgart, 1938; *Chem. Abstracts*, **26**, 2017 (1932).

[19] Kuhn and Wieland, *Ber.*, **73**, 962 (1940).

Adsorbents are able to take up relatively large particles. For example, bacteria can be taken up on many adsorbents.[20] Ore flotation phenomena probably also belong in this classification.

5. Mobile Interfaces

Many interesting separations can be carried out using a mobile interface for the adsorption.[21] The possibilities inherent in such applications are very great. As mentioned in previous chapters, these interfaces are likely to be much more homogeneous, in the plane of the surface, than the immobile ones, thus more reproducible and more predictable. They should be more homogeneous chemically, and, lacking in edges and corners, they should also be more homogeneous energetically. This does not mean that such surfaces, as found in foams and emulsions, would be lacking in strong chemical or physical effects. The use of foams for separations has been reviewed by L. Shedlovsky.[21] Dubrisay and others have reported on separations using foam,[21] and King[22] has shown that stable foams may be formed with organic liquids.

III. DECOLORIZATION

In industrial as in laboratory practice decolorization is often carried out by adsorption as a purification step preparatory to the isolation of a desired product. One of the largest uses of charcoal is in decolorizing sugar sirup as a step in preparing pure crystals.[23] Another large use is in the water purification industry.[24] Extremely large quantities of fuller's earth and other adsorbents are used in purifying petroleum products.[25] In the laboratory adsorption is used for similar purposes: to remove impurities, especially those which may inhibit crystallization or produce foaming, and to produce a clear liquid preparatory to distillation or other manipulations.[26]

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[20] Bechhold, *Kolloid-Z.*, 23, 35 (1918). Lasseur, Dombray, and Palgen, *Trav. lab. microbiol. faculté pharm. Nancy,* 7, 117 (1934); *Chem. Abstracts,* 30, 6033 (1936). Oksent'yan, *Microbiology U. S. S. R.*, 9, 3 (1940); *Chem. Abstracts,* 34, 6319 (1940).

[21] Shedlovsky, L., *Ann. N. Y. Acad. Sci.*, 49, 279 (1948).

[22] King, E. G., *J. Phys. Chem.*, 48, 141 (1944).

[23] V. R. Deitz, *Bibliography of Solid Adsorbents.* J. M. Brown, Revere Sugar Refinery, Charlestown, Mass., 1944.

[24] J. R. Baylis, *Elimination of Taste and Odor in Water,* McGraw-Hill, New York, 1935. J. W. Hassler, *Active Carbon, The Modern Purifier,* Industrial Chemical Sales Division, West Virginia Pulp and Paper Co., New York, 1941.

[25] C. L. Mantell, *Adsorption.* McGraw-Hill, New York, 1945.

[26] A. A. Morton, *Laboratory Technique in Organic Chemistry.* McGraw-Hill, New York, 1938.

The directions given in laboratory procedure for bringing about decolorization often call for the use of concentrated solutions and heat—sometimes even several hours of refluxing. Insofar as the decolorization proceeds by an ordinary adsorption process such directions are not necessarily realistic, even though conventional. Adsorption is usually fairly rapid, and it usually decreases with increase in temperature (except chemisorption, which may increase). The reasons sometimes given for the use of heat and long contacting are that adsorption is greater from more concentrated solutions, which in many cases can only be obtained in hot solvents; also that in many cases the purified product can be crystallized directly upon cooling the solution after removal of the adsorbent. The duration of contacting is justified by the recognition that adsorption reaches a maximum at equilibrium. It is often an advantage to be able to crystallize directly after decolorization; however, this and the other advantages are very often offset by the fact that in using a more concentrated solution both the product and the undesired adsorptive are concentrated, so that the adsorption of both may be improved. Furthermore, although the extent of adsorption increases (to the point of saturation of the adsorbent) with increase in concentration, the increase is relatively less at the higher concentrations. This effect is more noticeable the more curved is the isotherm, so that the advantage gained may even be negligible. Also, if the colored impurities are strongly adsorbed and the desired product weakly, so that the isotherm of the former is strongly curved compared with that of the latter, then adsorption of product may be improved by increased concentration relative to adsorption of impurities.

The most questionable feature of the conventional procedure is, however, the long heat treatment. Decolorizing agents are not to be thought of as chemically inert. There is an extensive literature on the catalytic properties of charcoal and other adsorbents.[27-31] Some of the reactions are gathered into Table VII-4. Many of these reactions do not require heat.

It is quite likely that many decolorizations are not purifications in the sense that they might at first appear to be. Some charcoals are known to

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[27] Warburg and Negelein, *Biochem. Z.* **113**, 257 (1921). Warburg, *ibid.*, **136**, 266 (1923). Negelein, *ibid.*, **142**, 493 (1923).

[28] Baur, *Helv. Chim. Acta,* **5**, 825 (1922). Wunderly, *ibid.*, **15**, 721 (1932); **16**, 515. 1009 (1933); **17**, 523 (1934). Baur and Schindler, *ibid.*, **18**, 1147 (1935). Further references in J. W. Hassler, *Active Carbon, The Modern Purifier,* West Virginia Pulp & Paper Co., New York, 1941.

[29] Tiselius, *Arkiv Kemi, Mineral. Geol.,* **B15**, No. 6 (1941). Schramm and Primosigh, *Ber.,* **76**, 373 (1943).

[30] Hesse, Reicheneder, and Eysenbach, *Ann.,* **537**, 67 (1938).

[31] Zechmeister, McNeely, and Sólyom, *J. Am. Chem. Soc.,* **64**, 1922 (1942).

possess strong reducing action—possibly because of adsorbed carbon monoxide. Others are actually oxidizing agents, perhaps through the agency of adsorbed oxygen.[32] Decolorization of unsaturated substances may be produced by reduction, or by oxidation to smaller fragments.

TABLE VII-4

A Few Reactions* Which May Occur on Adsorbents (see also Chapter VIII)

Reaction	Substance	Adsorbent
Isomerization	Olefins of types $RR'C{=}CH_2$ and $RR'C{=}CHR''$	Silica gel at room temp.[a]
Polymerization, etc.	Acetone to diacetone alcohol (aldol reaction)	Alumina[b]
	Reactions of olefins	Silica gel[c]
Acetal formation	Rhodin g trimethyl ester in methanol	Talc[d]
Hydrolysis	Acyl groups from triglycerides	Alumina[e]
Splitting of alcohol	From synthetic pigments	Alumina[f]
Oxidation	Vitamin C	Charcoals, some clays[g]
Catalase activity	In formation of indophenol	Charcoal[h]
Biological inactivation	Vitamin K	Magnesia and alumina[i]
Colorations	Vitamin A	Clays and acid earths[j]
	Amines and phenol	Clays, silica gel, Permutit, etc.[k]
	Amines (77 examples)	Bentonite, fuller's earth, kaolin[l]
	Aromatic amines	Acid clays[m]
	Triphenylmethane and other dyestuffs	Polar adsorbents from nonpolar solvents[n]
	In sugar sirups which are being decolorized	Bone charcoal[o]
Decolorizations	Removal of color from pure colored substances	Polar adsorbents[p]

* This table does not by any means cover all possible reactions, or all observations of any reaction.

[a] Gallaway and Murray, *J. Am. Chem. Soc.*, **70**, 2584 (1948). [b] Hesse, Reicheneder and Eysenbach, *Ann.*, **537**, 67 (1938). [c] Mair, *J. Research Natl. Bur. Standards*, **34**, 435 (1945). [d] Fischer and Conrad, *Ann.*, **538**, 143 (1939). [e] Trappe, *Biochem. Z.*, **306**, 316 (1940). [f] Brockmann and Junge, *Ber.*, **76**, 1028 (1943). [g] Kuhn and Gerhard, *Kolloid-Z.*, **103**, 130 (1943). [h] Schwob, *J. Am. Chem. Soc.*, **58**, 1115 (1936); Schwob, Biegner, Carson, and Scott, *ibid.*, **64**, 2276 (1942). [i] Dam and Lewis, *Biochem. J.*, **31**, 17 (1937). [j] Mayer and Sobotka, *Science*, **102**, 158 (1945); these authors give a partial bibliography. [k] Eisenack, *Zentr. Mineral., Geol.*, **1938A**, No. 10, 305. [l] Hauser and Leggett, *J. Am. Chem. Soc.*, **62**, 1811 (1940). [m] Meunier, *Compt. rend.*, **217**, 449 (1943). [n] Weitz and Schmidt, *Ber.*, **B72**, 2099 (1939); Weitz, Schmidt, and Singer, *Z. Elektrochem.*, **46**, 222 (1940); Buu-Hoi and Cagniant, *Bull. soc. chim.*, **11**, 410 (1944). [o] Deitz, *Status of the Bone Char Research Project*, Natl. Bur. Standards, 1947, p. 19. [p] Weitz and Schmidt, *Ber.*, **B72**, 2099 (1939).

These reactions would probably be aided by heating. Loss of color to a solution in the presence of charcoal, then, does not necessarily imply adsorption.

Usually, decolorization can be effected by use of a suitable solvent and adsorbent, using as a guide some of the general principles derived in earlier chapters. For example, in a Bucherer hydantoin synthesis involving an oleyl side chain the reaction product was dark. Partial decolorization was obtained by overnight boiling of the mixture in alcoholic solution with charcoal. But even more prolonged treatment did not produce further decolorization, and the product did not crystallize well from the mixture. The alcohol was removed and a dilute solution in ether prepared. This was passed cold through a small amount of charcoal held on a wad of cotton in the stem of a funnel (a chromatographic procedure). Complete decolorization was quickly obtained. In this case the alcohol was not only a good solvent for the reaction products but was also probably well adsorbed, thus competing effectively with the colored substances for the surface of the charcoal.

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[32] Hassler, in footnote 4.

In general, then, if trouble is experienced in obtaining decolorization, the procedure should be tried out in the cold, using a solvent which is not too well adsorbed, and using a relatively small amount of adsorbent to which the mixture is applied in a countercurrent manner.

IV. ADSORBENTS

Several compilations of adsorbents are available.[33] The following text and tables list adsorbents and their manufacturers and give some of the characteristics of the types of adsorbents. This cannot be considered a complete list because the number of adsorbents continually changes. Also, references to substances which may have special uses as adsorbents are often difficult to find. Almost any finely divided powder has potential value as an adsorbent. This list is an arbitrarily selected group of adsorbents which seem to be frequently referred to in the literature. It is not meant to imply that adsorbents not found in these tables are without value, or that any of these are better than others. It would be most difficult to make such judgments, and they would probably have no general value. For a bibliography covering the uses of these adsorbents up to 1942 see Deitz.[33] Strain[33] has listed some further uses. No explicit table of uses is listed here, since this need is filled by the articles by Strain[33] and the compilation by Dietz[33] and the monographs by Zechmeister and Cholnoky[33] and by Strain.[33]

[33] Applezweig, *Ann. N. Y. Acad. Sci.*, 49, 295 (1948). W. W. Binkley and M. L. Wolfrom, "Chromatography of Sugars and Related Substances," *Scientific Report Series No.* 10, Sugar Research Foundation, Inc., N. Y., 1948. V. R. Deitz, *Bibliography of Solid Adsorbents*, J. M. Brown, Revere Sugar Refinery, Charlestown, Mass., 1944. Dietz, *Ann. N. Y. Acad. Sci.*, 49, 315 (1948). H. H. Strain, *Chromatographic Adsorption Analysis*, Interscience, New York, 1945; *Anal. Chem.*, 21, 75 (1949); 22, 41 (1950). L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography*, Wiley, New York, 1943. See also under various headings in *Chemical Industries*, "Buyers Guide Section," 1948.

1. Aluminas and Related Materials (Table VII-5)

Aluminas suitable for use as adsorbents are usually made by partial dehydration of the hydroxide, which may be prepared by hydrolysis or neutralization of the salts. "Fibrous alumina"[34] is prepared from the cleaned metal by amalgamating it, and reacting with water, water vapor, or steam. Alumina, which is active as an adsorbent, always contains some water. Moreover it should not be reactivated at too high a temperature, because if all the water is driven off structural changes occur ("sintering") and the alumina loses activity. Brockmann and Schodder[35] set up an arbitrary gradation of activities of alumina based on the chromatographic separation of certain dyestuffs; a highly active commercial alumina was deactivated to certain degrees by exposing it to moisture for a given time.

TABLE VII-5
Aluminas and Related Materials Suitable as Adsorbents

Substance	Source
"Activated Alumina," Grade A, −80 mesh	Aluminum Ore Company, East St. Louis, Ill.
Aluminum oxide	Laboratory supply houses
Alumina, activated	Fisher Scientific Co., Eimer and Amend, N. Y.
Aluminum oxide. Reagent: "Suitable for Chromatographic Adsorption"	Merck and Company, Rahway, N. J.
"Driocel" (prepared from bauxite)	Attapulgus Clay Co., Philadelphia, Pa.
"Fluorite" (prepared from bauxite)	Floridin Company, Inc., Warren, Pa.
"Hydralo" (an activated alumina)	Baker Chemical Co., Phillipsburg, N. J.
"Porocel" (prepared from bauxite)	Porocel Corp., Philadelphia, Pa.

A typical analysis of "Activated alumina,"[36] grade A, is Al_2O_3 92%, loss on ignition 7%, $Na_2O < 1\%$, $SiO_2 < 0.1\%$, $Fe_2O_3 < 0.1\%$, $TiO_2 < 0.01\%$. The sodium is combined with the alumina and silica, and is not leachable.

Alumina has enjoyed the position for some time as the first choice for chromatography of new mixtures. It has probably been more used than any other adsorbent. It is a good adsorbent for most substances (with the proper solvents), has a large capacity, is white, insoluble, reasonably chemically inert (though the surface of the ordinary alumina gives a basic reaction), and readily obtainable. Alumina is, in fact, a very versatile adsorbent.

Alumina can be made to exchange anions or cations with suitable preliminary treatment. Kuhn and Wieland[37] prepared an anion adsorbent by treating commercial alumina as a slurry in water, with 2 *N* hydrochloric acid with thorough mixing, to a distinct Congo red reaction. The alumina was then separated and digested with distilled water until the wash liquid just gave a weak violet color with sensitive Congo red paper. On this adsorbent these investigators were able to separate (chromatographically) a physiologically active pantothenic anion. This substance could not be taken up on sulfuric acid treated adsorbent because the sulfate ion was more strongly adsorbed to the alumina. It could be eluted with alkali, which led these workers to set up the adsorption series for the acid-treated alumina: $Cl^- <$ active anion $< SO_4^{--} < OH^-$. Alumina may also be used as a cation exchanger, as has been shown by Schwab and Jockers.[38] Some of the physical and other properties of alumina and related substances are discussed by Heinemann, Krieger, and McCarter,[39] and by Krczil, and in other places.[40] The exchange capacity of alumina is low: *ca.* 0.01 meq./g.

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[34] Wislicenus, *Kolloid-Z.*, **100**, 66 (1942). Norberg, Auerbach, and Hixon, *J. Am. Chem. Soc.*, **67**, 342 (1945).

[35] Brockmann and Schodder, *Ber.*, **74**, 73 (1941).

[36] "Activated Alumina" is a registered trade mark of the Aluminum Ore Co.

2. Charcoals and "Carbons" (Table VII-6)

The term "carbon" is widely used in industry to refer to activated charcoals which may contain considerable ash. The use of this term is apparently based on the observation that when the carbon is burned off a decolorizing "carbon" such as bone charcoal, which may contain 90% ash, the ash residue shows little or no decolorizing power. The charcoals and carbons run the gamut in composition from nearly pure carbon (purified graphites and sugar charcoals) to charcoals containing approximately 90% ash (bone chars). Ogawa[41] determined the elementary composition of a sugar charcoal to be C 95.2–95.3, H 0.7, O 4.0–4.1%. Mantell[42] has given an analysis of American bone char (before use) as carbon 9.30, sand, etc. 0.42, tricalcium phosphate 75.00, calcium carbonate 6.23, calcium sulfate 0.08, calcium sulfide 0.01, ferric oxide 0.23. Bone char usually contains combined nitrogen and some moisture. Charcoals from animal and vegetable sources retain some of the cellular structure of the

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[37] Kuhn and Wieland, *Ber.*, 73, 962 (1940).

[38] Schwab and Jockers, *Naturwissenscaften,* 25, 44 (1937); *Angew. Chem.*, 50, 691 (1937). Graham and Horning, *J. Am. Chem. Soc.*, 69, 1214 (1947).

[39] Heinemann, Krieger, and McCarter, *Ind. Eng. Chem.*, 38, 839 (1946).

[40] F. Krczil, "Aktive Tonerde. Ihre Herstellung und Anwendung," in *Sammlung chemischer und chemisch-technischer Vorträge, Neue Folge,* Heft 41, Enke, Stuttgart, 1938; *Chem. Abstracts,* 26, 2017 (1932). C. L. Mantell, *Adsorption,* McGraw-Hill, New York, 1945; *Technical Literature,* Aluminum Ore. Co., East St. Louis, Ill.

[41] I. Ogawa, *Biochem. Z.*, 172, 249 (1926).

[42] C. L. Mantell, *Adsorption.* McGraw-Hill, New York, 1945, p. 101.

TABLE VII-6
Carbon,[a] Charcoals, and Carbonaceous Adsorbents

Substance	Source
Activated charcoals from coal	Pittsburgh Coke and Chemical Co., Pittsburgh, Pa.
Blood charcoal	Laboratory supply houses
Bone charcoal (from pyrolysis of bones)	American Agricultural Chemical Co., Detroit, Mich. Armour and Co., Atlanta, Ga. Baugh & Sons Co., Philadelphia, Pa. Consolidated Chemical Industries, New York, N. Y. Laboratory supply houses
Carbon blacks	Sources and characteristics are listed by L. H. Cohan, *Chem. and Eng. News*, **23**, 2078 (1945).
Cliffchar (from wood charcoal)	Cliffs-Dow Chemical Co., Marquette, Mich.
Columbia Activated Carbons (from hard nut shells, such as coconut)	Carbide & Carbon Chemicals Corp., New York, N. Y.
Darco carbons: Darco S-51 (from lignite) Darco G-60 (from wood) Darco K (from wood, chemical activation) Hydrodarco (from lignite)	Darco Corp., New York, N. Y.
Eponit (a European product)	American Norit Company, Inc., Jacksonville, Fla.
Graphites	Acheson Colloids Corp., Port Huron, Mich. Joseph Dixon Crucible Co., Jersey City, N. J.
Hydrodarco, see *Darco carbons* above	
Minchar carbons (from carbonaceous slate)	Minchar Manufacturing Co., Elmira N. Y.
Norit carbons (from pine-wood charcoals)	American Norit Co., Inc., Jacksonville, Fla. Laboratory supply houses
Nuchar carbons (from paper-pulp waste liquors)	West Virginia Pulp & Paper Co., New York, N. Y.
Sponge charcoal (burnt sponge)	Laboratory supply houses
Suchar carbons (from paper-pulp waste liquors)	West Virginia Pulp & Paper Co., New York, N. Y.
Sugar charcoals (from carbonized sugars)	Laboratory supply houses
Weschar (from lignite)	Western Filter Co., Denver, Col.

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[a] The term "carbon" is often used to mean an activated charcoal, which may contain considerable ash.

original material unless they have been graphitized by excessive heating.

Even charcoals made from recrystallized sucrose or dextrose contain ash. This ash may be removed, at least to some extent, by the method of Miller.[43] The charcoal, ground to pass a 300-mesh sieve, is mixed in a platinum vessel with concentrated hydrofluoric acid to form a thin paste. This is warmed gently until most of the acid has been driven off and is then heated until the hydrofluoric acid is completely removed. The adsorbent is then boiled with concentrated hydrochloric acid, the suspension diluted, and filtered in a Büchner funnel through hardened filter paper. The treatment with hydrochloric acid is repeated. The charcoal is then washed by repeated digestion with distilled water, dried, and ignited in the absence of air. The whole process is repeated until the desired purity is attained. The fine grinding is an essential. Miller gave the following examples of reduction of ash content: with blood charcoal the original ash content of 8.39 was reduced by three treatments to 0.06%; with Norit, the original 6.47% was reduced to 0.04% in two treatments; with activated sugar charcoal the initial ash content of 0.1% was reduced to 0.00% by one treatment. Miller[44] made an extensive study of purified charcoals from different sources and found them to become all much alike in some ways with purification.

A great deal has been written on the nature of the charcoal surface and the methods of modifying it. The surface can be modified by suitable treatments so that it is organophilic or hydrophilic,[45] Bartell and Lloyd[46] have prepared a charcoal, by activating purified sugar charcoal in a highly oxidizing atmosphere below 150°C., which approached the behavior of hydrophilic silica in its adsorptive properties; it gave only negatively charged particles when suspended in water. Their "high-temperature charcoal," activated near 1000°C., behaved as an organophilic adsorbent and on suspension in water showed both positively and negatively charged particles. The extensive work which has been done with carbonaceous adsorbents cannot be discussed here.[47]

3. Clays and Related Substances (Table VII-7)

The clay minerals comprise a wide variety of substances some of which are, or may be converted into, adsorbents. The minerals are crystalline substances of colloidal dimensions which show exchange properties to varying degrees. The behaviors of clays are related to the size, shape, and composition of the particles present, and to their exchange properties.[48] The size of the particles being within colloidal dimensions, the substances show relatively large surface areas. A mica from soil may have a surface area of some 60 square meters per gram, and a kaolinite 80 M^2/g.[49] Some natural clays will have particles larger than others, and the size can always be changed by physical and chemical treatment in activation and other processes. The shapes of the crystalline particles can be shown by electron microphotographs.[50] Kaolinites and some bentonites are composed of platelets. Montmorillonite is composed of platelets. Attapul-

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[43] E. J. Miller, *J. Phys. Chem.*, **30**, 1031 (1926).

[44] E. J. Miller, *J. Phys. Chem.*, **30**, 1162 (1926).

[45] Kolthoff, *J. Am. Chem. Soc.*, **54**, 4473 (1932).

[46] Bartell and Lloyd, *J. Am. Chem. Soc.*, **60**, 2120 (1938).

[47] For characteristics and sources of carbon blacks see: Cohan, *Chem. Eng. News*, **23**, 2078 (1945) (111 references); and "The Surface Area of Colloidal Carbons," *Columbian Colloidal Carbons*, Vol. III, Columbian Carbon Co., New York, 1942.

TABLE VII-7

Clays, Earths, Bentonites, etc. Used as Adsorbents

Substance	Source
Attapulgus clay products, Attapulgite	Attapulgus Clay Company, Philadelphia, Pa.
Bleaching Clay No. 260	Industrial Minerals & Chemical Co., Berkeley, Cal.
Filtrol products (many types made) Desiccite (a dehydrated bentonite) Filtrols (activated bentonite preparations) Neutrols (activated clays with a neutral reaction)	Filtrol Corp., Los Angeles, Cal.
Floridin products Diluex (a selected fine-mesh fuller's earth) Floraid (an adsorbent filter aid) Florex xxx (an extruded fuller's earth) Floridin (a fuller's earth) Florigel (a hydrated fuller's earth) Florisil (a magnesium trisilicate analytical adsorbent)	Floridin Co., Inc., Warren, Pa.
Fuller's earths (bleaching clay)	Laboratory supply houses
Infusorial earth	Laboratory supply houses
Kaolinite	Laboratory supply houses
Lloyd's reagent (prepared from fuller's earth)	Eli Lilly & Co., Indianapolis, Ind.
Sinclair Earth (a fuller's earth)	Sinclair Refining Co., New York, N. Y.
Talc, purified powder, U. S. P.	Laboratory supply houses
Volclay bentonites (a variety of types are made)	American Colloid Co., Chicago, Ill.

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[48] Hauser, *Chem. Revs.*, 37, 287 (1945).

[49] Hendricks, *Ind. Eng. Chem.*, 37, 625 (1945).

[50] Shaw, *J. Phys. Chem.*, 46, 1032 (1942). Marshall and Caldwell, *J. Phys. & Colloid Chem.*, 51, 311 (1947).

gite is made up of fibrous particles. In composition, these substances are silicates. The kaolinites are aluminosilicates. The bentonites are also aluminosilicates, but more complex. They are of different types: some have sodium, others calcium as the chief exchangeable cation, but potassium and magnesium are also present. The behavior of these substances toward water, electrolytes, and organic liquids depends very much on their composition.[48]

The crystalline base-exchanging silicates have been classified by Hendricks[49] in terms of the site of the exchangeable ions. The original article should be consulted for the complete classification, which is not given here. Among those crystalline silicates with exchange sites within the structural framework are the zeolites. These have an open framework of interconnected channels, so that when an ion diffuses into the structure another can diffuse out, thus maintaining electroneutrality. The dimensions of these channels are different for different zeolites. Barrer[51] has used this property to divide zeolites into three classes which differ in the size of molecule that can be occluded by the particular zeolite. The cations required to balance the charges of these substances are located, along with their associated water molecules, in the interstitial spaces of the framework. The other class of crystalline silicate exchangers have the exchange site external to the structural framework. These fall into 3 subclasses: (*a*) the montmorillonite type of clay minerals, wherein the exchange sites are mostly on an inner surface accessible to swelling; (*b*) the micas (including glauconite) in which the exchange sites are at the limiting crystal surfaces; and (*c*) the kaolin minerals wherein only a limited part of the external surface supports exchange. In attapulgite, which falls between several classes, the fibrous structure leaves channels of cross-section about 3.7 by 6.0 A.[52] Molecules of considerable size can be admitted. In the natural clay these are largely filled with loosely held water and a relatively small proportion of mobile (exchangeable) cations. An attapulgite might show a base exchange capacity of 0.25 to 0.3 meq./g.[53] In the kaolinites the base-exchange occurs, so to speak, where the ionic lattice terminates, or where the platelets have been broken, so that an incomplete balancing of charge requires the presence of external ions.[54] The exchange capacity compared with the other minerals is somewhat low, for this reason. Thus the kaolinite referred to above, with a surface area of some 80 square meters per gram shows an exchange capacity of about 0.12 meq./g. An attapulgus clay might show a surface area of 170 square meters per gram (see Table IX-1). The zeolite exchangers are referred to further in Chapter IX.

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[51] Barrer, *J. Soc. Chem. Ind.*, 64, 130T, 133T (1945). Barrer and Belchetz, *ibid.*, 64, 131T (1945).

[52] Marshall and Caldwell, *J. Phys. & Colloid Chem.*, 51, 311 (1947).

[53] Hauser, *Chem. Revs.*, 37, 287 (1945).

[54] Hendricks, *Ind. Eng. Chem.*, 37, 625 (1945).

Fuller's earth and other clays are used in extremely large quantities for bleaching, decolorizing, catalysis, and a myriad of other applications. In using these substances in the laboratory for analytical work it may be necessary to wash off traces of oily material which may be present.[55] Sometimes a prewash (see below) with an organic solvent can improve the behavior of the adsorbent. Thus, Binkley and Wolfrom[56] prewash Florex xxx with an azeotropic mixture of dioxane and water.

4. Diatomaceous Earths. Filter Aids (Table VII-8)

Ever since their introduction by Strain[57] in this application the diatomaceous filter aids have seen increasing use in chromatography. They have been used in two applications. The most important use is for improving the solvent flow rate through columns of adsorbent. The filter aid is mixed with the finely powdered adsorbent in a suitable ratio. LeRosen[58] found an inverse linear relation between the volume fraction of silicic acid in mixtures with Celite 535 and the $\log_{10}$ of the rate of flow of developing solvent. The use of a filter aid mixed in with the adsorbent also makes it easier to pack the adsorption columns uniformly. Using a standard method of packing in which the adsorbent was poured slowly into the tube under the full vacuum of a water pump, and the tube then tapped vigorously, LeRosen[58] found that the percentage of the tube volume occupied by the adsorbent increased linearly with the weight fraction of

TABLE VII-8
Diatomaceous Filter Aids

Substance	Source
Celites (diatomaceous filter aids) Celite analytical filter aid; Filter-Cel; Hyflo Super-Cel; Super-Cel	Johns-Manville Corp., New York, N. Y.
Clara Cel (diatomaceous filter aid)	Tamms Silica Co., Chicago, Ill.
Dicalites (diatomaceous filter aids) There are some 9 types of Dicalites suited to various applications	Dicalite Company, New York, N. Y.

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[55] Zechmeister, McNeely, and Sólyom, *J. Am. Chem. Soc.*, **64**, 1922 (1942).

[56] W. W. Binkley and M. L. Wolfrom, "Chromatography of Sugars and Related Substances," *Scientific Report Series No. 10,* Sugar Research Foundation, Inc., New York, 1948.

[57] Strain, *J. Biol. Chem.*, **105**, 523 (1934).

[58] LeRosen, *J. Am. Chem. Soc.*, **67**, 1683 (1945).

silicic acid in admixtures with Celite 535. The ratio of filter aid to adsorbent for a given new application is usually determined by trial. Wilkes[59] has recommended Celite 545 as a high-speed filter aid.

Filter aids may be used as adsorbents. Gallagher, Koch, and Dorfman[60] adsorbed the male sex hormone from acidified urine, with Dicalite. Estrogenic substances were not appreciably adsorbed. The adsorptive power of filter aids is relatively low, and usually does not interfere with their use for speeding flow. In new applications, however, possible adsorption by the filter aid should be taken into account and tested for.[59,61]

Filter aids sometimes contain impurities which are washed off by developer solvents.[62] A yellow impurity, observed by Wilkes,[59] was removed by prewashing the adsorption column with water or methanol.

5. Ion Exchange-Resins and Zeolites

For a listing and discussion of these substances, see Chapter IX. The terms are usually used for substances which are fairly massive in their particle size—that is, not colloidal—and which have a relatively high capacity for ions. The clays, many of which are also capable of ion exchange, are thus excluded.

6. Silicas and Silica Gels (Table VII-9)

These substances are coming into considerable use in chromatography. Silica gel has been used extensively in the separation of paraffin, naphthene, and aromatic hydrocarbon fractions by Mair and his coworkers.[63]

TABLE VII-9
Adsorbent Silicic Acids and Silica Gels

Substance	Source
"Santocels" (silica aerogels)	Monsanto Chemical Co., Boston, Mass.
Silica gel (a number of grades are produced)	Davison Chemical Co., Baltimore, Md.
	International Filter Co., Chicago, Ill.
Silica, or silicic acid, reagent grade	Laboratory supply houses

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[59] Wilkes, *Ind. Eng. Chem., Anal. Ed.*, 18, 329 (1946).

[60] Gallagher, Koch, and Dorfman, *Proc. Soc. Exptl. Biol. Med.*, 33, 440 (1935–36).

[61] Strain, Manning, and Hardin, *Biol. Bull.*, 86, 169 (1944).

[62] Strain, *Nature*, 137, 946 (1936). Thompson, Ewan, Hauge, Bohren and Quackenbush, *Ind. Eng. Chem., Anal. Ed.*, 18, 113 (1946).

[63] Mair and Forziati, *J. Research Natl. Bur. Standards*, 32, 151, 165 (1944). Mair, *ibid.*, 34, 435 (1945). Mair, Gaboriault, and Rossini, *Ind. Eng. Chem.*, 39, 1072 (1947).

A typical analysis of a gel prepared for chromatographic use by the Davison Chemical Co. is, on the dry basis, 99.71% SiO_2, with traces of iron, aluminum, titanium, calcium, sodium, zirconium, and other elements present. The screen analysis of the gel is given as on 100 mesh $< 5\%$; on 200 $< 20\%$; on 325 $> 75\%$. The total volatile material: 6.0%. Santocel is a silica aerogel[64] made in several grades. The approximate analysis for most grades is: SiO_2, 81.5–90%; volatile (water, alcohol, and acetaldehyde) 7–10%; Na_2SO_4, 8.5–9.5%; Al_2O_3 and Fe_2O_3, 1%. The substance is light in weight and has a large surface area (Table VII-1).

Silica, or silicic acid, reagent grade, is finding a great many applications in chromatography. The substance is inert and a good adsorbent for polar substances. It was found in Zechmeister's laboratory[65] that the strength of the adsorbent can be influenced by prewashing. The prewashing, which is most effective, appears to remove water from the adsorbent.[66] The order of increasing adsorptive power produced by prewashing has been given by Schroeder[65] as follows, where V ml. is the volume of solvent which is required to wet completely the column of adsorbent; alcohol-prewashed adsorbent (V ml. absolute alcohol followed by $2V$ ml. ligroin) less active than unprewashed adsorbent, which is less active than ether-prewashed adsorbent (V ml. ether, $2V$ ml. ligroin) which is less active than acetone–ether-prewashed adsorbent ($0.2V$ ml. ether, V ml. 1:1 acetone–ether, $0.8V$ ml. ether, V ml. ligroin). The acetone–ether prewash yields an adsorbent of the same activity as is produced by heating the silicic acid at 200°C. for about 40 minutes. LeRosen[66] found that Merck reagent silicic acid was very responsive to this activation by prewashing technique.

7. Additional Inorganic Substances Used as Adsorbents (Table VII-10)

The substances listed under this heading, with a few exceptions, are not as frequently used as those described previously. The exceptions are Magnesol and Silene EF, which have found much use in the separation of sugars and their derivatives,[67] and Micron brand of magnesium oxide, which Strain has found very useful with plant pigments.[68]

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[64] Kistler, Fischer, and Freeman, *J. Am. Chem. Soc.*, 65, 1909 (1943).

[65] Schroeder, *Ann. N. Y. Acad. Sci.*, 49, 204 (1948).

[66] LeRosen, *J. Am. Chem. Soc.*, 67, 1683 (1945).

[67] W. W. Binkley and M. L. Wolfrom, "Chromatography of Sugars and Related Substances," *Scientific Report Series No. 10*, Sugar Research Foundation, Inc., New York, 1948.

[68] H. H. Strain, *Leaf Xanthophylls*, Carnegie Inst. Washington, Washington, D. C., 1938; *Chromatographic Adsorption Analysis*, Interscience, New York, 1945.

TABLE VII-10

Additional Inorganic Substances Useful as Adsorbents

Substance	Source
Alba-floc (a finely divided calcium sulfate)	U. S. Gypsum Co., Chicago, Ill.
Barium carbonate (a somewhat better adsorbent than calcium carbonate)	Laboratory supply houses
Calcium carbonate (U. S. P. precipitated chalk)	Laboratory supply houses
Calcium hydroxide (lime, from slaking the oxide)	Laboratory supply houses
Shell brand lime	Braun Chemical Co., Los Angeles, Cal.
Defluorite (a tricalcium phosphate preparation)	Aluminum Corporation of America, Pittsburgh, Pa.
Drierite (anhydrous calcium sulfate)	W. A. Hammond Drierite Co., Xenia, Ohio
Glass, porous	Corning Glass Company, Corning, N. Y.
Glass, spheres	Method of preparation described by Urbanic and Damerell, *J. Phys. Chem.*, **45**, 1245 (1941)
Gypsum, hydrated	Laboratory supply houses
Magnesium carbonate	Laboratory supply houses
Magnesium citrate	Laboratory supply houses
Magnesium oxide	Laboratory supply houses
Micron brand of magnesium oxide, No. 2641	Westvaco Chlorine Products Corp., New York, N. Y.
Magnesium Trisilicate No. 34	Philadelphia Quartz Co., Ltd., Berkeley, Cal.
Magnesol (synthetic hydrous magnesium trisilicate)	Westvaco Chlorine Products Corp., New York, N. Y.
Rutiles (79 to 98.5% titanium oxide)	National Lead Co., South Amboy, N. J. The Titanium Alloy Mfg. Co., Niagara Falls, N. Y.
Silene EF (synthetic, hydrated calcium silicate)	Columbia Chemical Div., Pittsburgh Plate Glass Co., Barberton, Ohio
Sodium carbonate, anhydrous	Laboratory supply houses
Titania adsorbent (made from the tetrachloride)	Directions for making given by Johnson, *Diss., The Catholic Univ. of Amer. Biol. Ser.*, 29 (1938).
Titanium oxide (TiO_2)	National Lead Co., South Amboy, N. J. The Titanium Alloy Mfg. Co., Niagara Falls, N. Y.
Zinc oxide	Laboratory supply houses Pigment manufacturers
Zirconium silicate (zircon)	The Titanium Alloy Mfg. Co., Niagara Falls, N. Y.

8. Organic Substances Used as Adsorbents (Table VII-11)

A number of organic substances have found use as adsorbents, particularly in applications where mildness of action is desired. Filter paper pulp may be purchased, or it may be prepared by boiling and shredding filter paper scraps (with a hand or mechanical beater). Filter paper pulp makes an effective filter aid for charcoal adsorption columns.[69] It can be used as a support for one phase in the partition chromatogram (Chapter X). Boscott[70] has suggested that cellulose acetate ($^1/_4$ in. staple filaments) can be used in this way for supporting the butanol phase in partition chromatography. The polymer is swelled with butanol at 50° for 30 min. and then the excess solvent is removed by filtration, pressing, and washing with saline. Starch has also been used in partition chromatography.[71] Detailed directions for preparing the starch column (with potato starch) are given by Stein and Moore.[72] Starch also can act as an adsorbent.[73]

TABLE VII-11
Some Organic Substances Used as Adsorbents

Substance	Source
Cellulose. Filter paper pulp	Laboratory supply houses
Inulin	Laboratory supply houses
Lactose	Laboratory supply houses
Solka-Floc BW 200 (purified wood cellulose)	Brown Co., Berlin, N. H.
Sucrose (confectioner's sugar contains about 3% starch)	Confectioner's multiple x sugar. Grocery stores
Starches	
corn and rice starch	Stein, Hall & Co., Inc., New York, N. Y.
white potato starch	Amend Drug and Chemical Co., Inc., New York, N. Y.

Confectioner's xxxxx powdered sugar is a satisfactory adsorbent for many separations.[74] The substance is easily available and not very expensive. Inulin and lactose are also used as adsorbents.

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[69] Wachtel and Cassidy, *J. Am. Chem. Soc.,* 65, 665 (1943).

[70] Boscott, *Nature,* 159, 342 (1947).

[71] Elsden and Synge, *Biochem. J.,* 38, ix (1944). Synge, *ibid.,* 38, 285 (1944).

[72] Stein and Moore, *J. Biol. Chem.,* 176, 337 (1948).

[73] Lehrman, *J. Am. Chem. Soc.,* 64, 2144 (1942). Moore and Stein, *Ann. N. Y. Acad. Sci.,* 49, 265 (1948).

[74] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography,* Wiley, New York, 1943. H. H. Strain, *Chromatographic Adsorption Analysis,* Interscience, New York, 1945.

V. STANDARDIZATION AND EVALUATION OF ADSORBENTS

The standardization of an adsorbent can be carried out only on the basis of an operational definition of standardization. Neglect of this fact has led to many difficulties, contradictions, and confusions.[75] Recognition of this fact is bringing some progress in the matter. An adsorbent can be standardized on the basis of its capacity *for* some substance, or type of substance; but it cannot be standardized on the basis of some concept called "its capacity". An adsorbent can be standardized also on the basis of selectivity *between* given pairs (or larger numbers) of substances, but not just on the basis of its "selectivity." The standardization involves a comparison of the adsorbent in question with some other which shows a known degree of standard behavior, or with the defined properties which are accepted as standard. In any case, if a standard is set up, it must be arbitrary to some extent. The alternative is not to set up a standard, but to describe the adsorbent in terms related to its function. This gives a means of evaluating the adsorbent, and is in many ways a more profitable procedure than standardization, but it also requires more knowledge of the behavior of the adsorbent, and this, for practical reasons, is often lacking, or even unobtainable.

1. General Adsorbents

One of the difficulties met in evaluating adsorbents, as for industrial use, is that they are often used to adsorb substances of unknown chemical nature, such as the "color" of molasses solutions, or the "odor" and "taste" of treated water. Since the natures of the substances to be adsorbed are not known, a standard substance has to be taken, such as a "standard molasses solution" in sugar sirup decolorization, against which the adsorbents can be tested. An alternative is to use a "standard reference adsorbent" against which other adsorbents can be tested *via* any molasses solution. A great deal of work has been done to find some pure, easily analyzed substance which can be used as a substitute for these ill-defined "colors" and "odors." Iodine in KI has been widely used, since the brown-colored solutions can be decolorized and the extent of adsorption easily checked by titration with thiosulfate. Hassler[76] states that the iodine adsorption test applied to charcoals seems to be indicative more of the ability of the adsorbent to remove odors and flavors than to remove color bodies. Permanganate solutions have also

[75] Herbst, *Kolloid-Z.*, 38, 314 (1926).

[76] J. W. Hassler, *Active Carbon, The Modern Purifier.* Industrial Chemical Sales Division, West Virginia Pulp and Paper Co., New York, 1941.

been used, as have methylene blue or ponceau red solutions. In testing the ability to remove "odor" and "taste" from water, phenol adsorption and adsorption of other pure substances have been investigated.[77] A fundamental, but by no means the only, weakness of these indirect tests is that there is no way of determining the correspondence between percent of color reduction in, say, molasses solution and the removal of a given percent of iodine from a stock solution. The tendency in applying adsorbents is more and more to test them on actual samples of the materials with which they are to be used, and to make the tests at a number of concentrations so as to avoid the errors of one-point comparisons.[78]

In testing adsorbents for laboratory use (decolorization and chromatography) the "activity" of the adsorbent and its "selectivity" are measured. The former usually implies avidity with which the adsorbent takes up an adsorptive, but it may be used to imply capacity of the adsorbent. Heat of wetting has been used by many investigators to evaluate adsorbents.[79,80] Attempts have then been made to correlate the observed values with adsorption behavior. Müller[80] prepared aluminas of four activities by adding different amounts of water to a strongly active preparation made by heating a commercial alumina. The activities of these adsorbents were measured by the amount of heat given off when 50 g. of the adsorbent at 0° was mixed with 65 cc. of developer liquid at 0° with slow stirring. Müller correlated increased activity as measured above with increased strength of adsorption for adsorptives. A choice of developer or eluent could be made on the basis of these measurements. Also it was possible to prepare adsorbents of intermediate activity by mixing high activity and low-activity aluminas. This allowed an adjustment of the activity of the adsorbent to the particular chromatographic problem. Heat of wetting is not necessarily a reliable guide to the activity of the adsorbent in the solvent (Chapter V).

Tests of capacity can be made by break-through experiments or by batchwise adsorption. In the former type the weighed adsorbent is placed as a bed, or column, in a tube, and the test solution is passed in until adsorptive at the foot of the column breaks through. The volume of "empty" liquid up to this point is the "break-through volume." In the latter type of experiment a weighed amount of adsorbent is shaken with a known amount of standard solution and the amount of adsorptive adsorbed is determined from the change in concentration of the solution. As an example of the latter measurement, Miller[81] defines a good grade of charcoal as one, 0.25 g. of which will, at equilibrium, adsorb about 50% of the benzoic acid from 100 cc. of a 0.02 *M* solution. (To ensure contact the charcoal is well mixed with the solution and the mixture is evacuated at a water pump to remove occluded gas from the charcoal.)

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[77] Helbig, *J. Am. Water Works Assoc.*, 30, 1225 (1938); 31, 1931 (1939). Hassler and McMinn, *Ind. Eng. Chem.*, 37, 645 (1945).

[78] C. L. Mantell, *Adsorption*. McGraw-Hill, New York, 1945.

[79] Sastri and Krishnaswami, *Quart. J. Indian Inst. Sci.*, 5, No. 2 (1942). Stone and Clinton, *Ind. Eng. Chem., Anal. Ed.*, 14, 131 (1942).

[80] Müller, *Verhandl. Ver. schweiz. Physiol.*, 21, 29 (1942); *Helv. Chim. Acta*, 26, 1945 (1943).

2. Chromatographic Adsorbents

Another method of testing adsorbents was used by Brockmann and Schodder.[82] Technical alumina was activated (dehydrated) by strong heating and then deactivated to controlled degrees by exposure to moist air. An arbitrary set of 5 degrees of activity was set up. The activities were judged by the ability of the given grade to make separations between various pairs of dyestuffs. There was some question, however, about the transferability of data such as these to mixtures of substances other than the dyestuffs. Kaufmann[83] suggested that the ability of an adsorbent to separate fatty acids should be tested on fatty acids. Lew, Wolfrom, and Goepp,[84] recognizing the arbitrary quality of the choice, set up a standard of good selectivity in work with sugars and derivatives as the ability to separate a mixture of sorbitol (D-glucitol) and D-mannitol.

Weil-Malherbe has suggested that the threshold volume (the breakthrough volume) per unit weight of adsorbent be used to compare adsorbents and eluents. Claesson[86] has found that the Langmuir equation describes fairly well the adsorption of a number of aliphatic substances on a number of charcoals from absolute ethanol. He writes this equation as:

$$a_i^0 = k_i c_i/(1 + l_i c_i)$$

where a_i^0 is the amount of the *i*th component adsorbed per gram of adsorbent at the equilibrium concentration c_i, and k and l are constants. In comparing isotherms of homologous fatty acids Claesson observed that this k increases in geometric progression with arithmetic increase in the chain length, giving the relation:

$$k = pq^n$$

where p and q are constants and n is the number of carbon atoms in the fatty acid (no alternation was observed in k). A relation of this type held reasonably well (with different constants) for ethyl esters, dibasic acids, and alcohols, and for five different charcoals. One charcoal showed rather large discrepancies.

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[81] Miller, *J. Phys. Chem.*, 30, 1162 (1926).

[82] Brockmann and Schodder, *Ber.*, 74, 73 (1941).

[83] Kaufmann, *Angew. Chem.*, 53, 98 (1940).

[84] Lew, Wolfrom, and Goepp, *J. Am. Chem. Soc.*, 68, 1449 (1946).

[85] Weil-Malherbe, *J. Chem. Soc.*, 1943, 303.

[86] Claesson, *Arkiv Kemi, Mineral. Geol.*, A23, No. 1 (1946).

Claesson suggested, then, that charcoals can be calibrated and compared for use with homologous series through these constants p and q. A charcoal with a larger q value has greater separating power than one with a smaller q value; a larger p value indicates greater adsorption than a smaller p value. The determination of the p and q values for a charcoal is possible from a single frontal analysis (Chapter X) of a mixture of two different fatty acids (see the original paper for the calculations), but is more accurately determined from the isotherms of two homologs. Homologs with quite widely different numbers of carbon atoms are taken. The isotherms are measured, and the data plotted as $1/a^0$ against $1/c$ for each homolog. A straight line plot indicates that the Langmuir isotherm is applicable to the data. The slope of this line is $1/k$ and the intercept on the $1/a^0$ axis is l/k. The constants can thus be obtained for the two homologs. Log k is then plotted against n, and the two points are connected with a straight line, from the slope of which log q can be obtained and log p from the intercept.

LeRosen[87] has made a somewhat different approach to the standardization and evaluation of adsorbents for chromatographic use. He has defined a number of terms the values of which can be used to characterize an adsorbent. These are, for measuring flow characteristics, V_c and T_{50}; for measuring packing in the column, S; and for measuring adsorption affinity, R. These terms are defined as follows: V_c is the velocity of flow of the developing solvent through the column when a constant value is reached. When the solvent is poured on the column the velocity of flow decreases but becomes constant soon after the solvent has reached the bottom of the column. The velocity of flow varied with the pressure difference between the ends of the column, inversely with the length of the column, and was more or less independent of the diameter of the column. V_c is measured as the velocity (mm./min.) at which the meniscus of the developer solution moves down the tube. A further investigation of the factors controlling V_c has enabled LeRosen,[88] through the concept of the permeability of the column of adsorbent, to calculate V_c for different values of pressure, column length, and solvent viscosity. The relation used is rewritten from the expression for the permeability of a porous solid derived from the Darcy law:[89]

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[87] LeRosen, *J. Am. Chem. Soc.*, 64, 1905 (1942).

[88] LeRosen, *Anal. Chem.*, 19, 189 (1947).

[89] M. Muskat, *Flow of Homogeneous Fluids through Porous Media.* McGraw-Hill, New York, 1937.

$$V_c = k(A/760\alpha)P/\eta L$$

k is the permeability in darcys, A the cross-sectional area of the column in square centimeters; α the interstitial volume of the column in milliliters per millimeter (determined experimentally); P the driving pressure in millimeters of mercury (the difference in pressure between the two ends of the column); η the viscosity of the solvent in centipoises; and L the length of the column in centimeters. Good agreement between calculated and observed V_c values was obtained.

The quantity T_{50} is defined as the time in seconds required for a solvent to penetrate 50 mm. into an initially dry column of adsorbent 9 × 75 ± 2 mm. in dimensions under the full vacuum of a water pump.[90] The column is prepared in a standard manner: the adsorbent is poured into the chromatographic tube under the vacuum of the water pump, and settling is aided by tapping the sides of the tube. The surface of the column is leveled without pressing down on the adsorbent. LeRosen found that, when columns of silicic acid were prepared with a filter aid diluent (silicic acid–Celite 535 mixtures), $\log_{10} V_c$ decreased linearly with the volume fraction of silicic acid, and $\log_{10} T_{50}$ increased linearly with the volume fraction of silicic acid.

The quantity S is the length of adsorbent column which will contain unit volume of solvent divided by the length of unfilled adsorption tube required to hold the same volume of solvent.[91] The ratio S is therefore a measure of the average packing in the column. LeRosen found S to vary along the column. With the silicic acid–Celite mixtures mentioned in the previous paragraph S increased linearly with the weight fraction of silicic acid.[90]

The adsorption affinity R is defined as the velocity (mm./min.) of movement of adsorptive zone divided by the velocity of flow of developing solvent (V_c).[91] R is thus the velocity of movement of the zone relative to that of the solvent, and is dimensionless. The measurement of R is made from the lower, sharper edge of the zone. In measurement of changes of zone depth the terms R_t and R_l are used for the R values of the trailing and leading edges of the zone.[90,92] LeRosen has shown that R is identical with the fraction $T_s/(T_a + T_s)$, where T_s is the average time that an adsorptive molecule spends in solution between each adsorption, and T_a the average time on the adsorbent.[90] With silicic acid–Celite mixtures, $(1-R)/R$ increases linearly with the volume fraction of silicic acid. R can be calculated with fair agreement with experiment from data obtained from isotherms.

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[90] LeRosen, *J. Am. Chem. Soc.*, **67**, 1683 (1945).

[91] LeRosen, *J. Am. Chem. Soc.*, **64**, 1905 (1942).

[92] LeRosen, *J. Am. Chem. Soc.*, **69**, 87 (1947).

These various quantities, then, can be used to evaluate, characterize, and standardize adsorbents. LeRosen[90] suggests that in many cases (but depending on the chromatographic problem) the following ranges of values are satisfactory: $V_c = 10–50$ mm./min.; $T_{50} = 20–100$ sec.; $R = 0.10–0.30$; and S, no special requirement.

VI. ACTIVATION OF ADSORBENTS

Activation processes for charcoals have been reviewed by many authors besides the few listed here.[93] In general, it would appear that high-temperature activation produces a charcoal which may be quite organophilic in its properties, while low-temperature activation, particularly in the presence of a strongly oxidizing atmosphere, produces a hydrophilic charcoal which may be made very hydrophilic indeed. In the activation of charcoal *very* high temperatures should be avoided, since above about 1100° graphitization, with loss in activity, takes place. Herbst[93] visualizes graphitization as a process in which the adsorption-active carbon molecules in the surface rearrange, mutually saturating each other, so that the charcoal becomes more compact and shows a higher specific gravity. If charcoal is to be used with oxidation-sensitive substances, it may be advisable to heat it to a high temperature and cool it in an inert atmosphere.[94]

In some applications charcoals need to be degassed before they show their highest capacity. The solvent, in such cases, seems unable to penetrate the air- or gas-filled capillaries.[95] The remedy is to subject the mixture of adsorbent and solution to vacuum (*cautiously*) with gentle boiling, or to evacuate the adsorbent (cautiously at first until most of the gas has been released), and release the vacuum with solvent vapors. This treatment is frequently recommended in directions for decolorization.

The activation of alumina and its deactivation have already been discussed. The chief caution here is not to heat the adsorbent too much. A temperature of 200° should not be exceeded.[96] The adsorbent dried at this temperature still contains some moisture (around 8%). To drive off all the moisture requires a temperature so high as to cause sintering and loss of activity of the porous adsorbent.

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[93] Herbst, *Kolloid-Z.*, 38, 314 (1926). Schilow, Schatunowskaja, and Tschmutow, *Z. physik. Chem.*, A149, 211 (1930). Roychoudhury, *J. Indian Chem. Soc.*, 8, 433 (1931). Bartell and Lloyd, *J. Am. Chem. Soc.*, 60, 2120 (1938).

[94] Holmes, Cassidy, Manly, and Hartzler, *J. Am. Chem. Soc.*, 57, 1990 (1935).

[95] Bauer, in Weissberger, ed., *Physical Methods of Organic Chemistry*. 2nd ed., Interscience, New York, 1949, Part I, p. 288.

[96] Milligan, *J. Phys. Chem.*, 26, 247 (1922).

Reproducible activation of silica gel has been discussed by Bartell and Almy.[97] The gel should probably not be heated above 300°. With Bartell and Almy's sample of gel the maximum activity was produced by heating two hours at 300°. Adsorbed water was still present and could be driven off at higher temperatures, but it appeared that under these conditions the gel structure collapsed. At any rate, the activity of the gel decreased. Mair[98] reactivated silica gel after using it to adsorb hydrocarbons by heating it to 180 to 200°C. in a slow stream of inert gas.

Activation of silicic acid was discussed above. It can be produced by prewashing the adsorbent, and can be regulated by the nature of the prewashing solvent.[99] LeRosen[100] has compared the behaviors of two silicic acids toward prewashing.

Much work has been done on the activation of adsorbents by coating them with metals,[101] fatty acids, and other substances.[102] This subject cannot be discussed here, nor can the interesting subject of activation by admixture of adsorbents.[103]

VII. RECOVERY OF ADSORBENTS

Most adsorbents can be recovered by washing off the adsorbed material and reactivating the adsorbent (see above). This is common industrial practice. Sometimes more drastic conditions are used. For example, spent bone char from sirup decolorizing is treated by washing with acid and alkali, and by other washes to remove some of the adsorbed materials, and the rest are selectively oxidized by kiln burning of the charcoal. A good bone char may withstand some 200 revivifications before being discarded.[104]

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[97] Bartell and Almy, *J. Phys. Chem.*, 36, 475 (1932).

[98] Mair, *J. Research Natl. Bur. Standards*, 34, 435 (1945).

[99] Schroeder, *Ann. N. Y. Acad. Sci.*, 49, 204 (1948).

[100] LeRosen, *J. Am. Chem. Soc.*, 67, 1683 (1945).

[101] Reyerson and Swearingen, *J. Phys. Chem.*, 31, 88 (1927). Reyerson and Cines, *ibid.*, 46, 1060 (1942).

[102] Acharya, *J. Indian Chem. Soc.*, 13, 723 (1936); 14, 188 (1937).

[103] Chowdhury and Pal, *J. Indian Chem. Soc.*, 7, 451 (1930).

[104] C. L. Mantell, *Adsorption*. McGraw-Hill, New York, 1945.

CHAPTER VIII

Chromatography (Tswett-Column Analysis, Chromatographic Adsorption Analysis, Differential Countercurrent Adsorption Analysis)

I. INTRODUCTION

Chromatography is a method of using adsorption in a differential countercurrent manner (Chapter VI) thus, most of the information gathered in this book has a bearing here. The chief use of some of this material is made in its application to chromatography, which is one of the most subtle and versatile analytical tools of the chemist.

Chromatography was invented by Tswett[1] in 1906 during his studies on the chemistry of chlorophyll. He named the method and classified it as a kind of adsorption analysis distinct from what might be called "conventional," or batchwise adsorption. He showed that the chromatographic method provides a powerful means for separating chemical substances. He also recognized that it could be used with a wide variety of adsorbents, solvents, and solutes, and that it was applicable not only to colored substances, but also to colorless materials.* He pointed out that one could use adsorbents which were chemically passive, or which produced some chemical action such as hydrolysis, reduction, or oxidation. A good deal of the general technique practiced today was outlined by Tswett. A history of the vicissitudes of the method from its inception to the present time may be found in a number of sources.[2,3]

In this chapter the method of chromatography will be described together with some of its apparatus. The adaptations necessary for dealing with various kinds of compounds, for standardizing the method, and for applying instruments to it will be discussed, together with some of the theory, and a section of the chapter will be devoted to manipulations. How to go about applying the method to a given problem is discussed in Chapter XI. The failings of the method will also be made apparent. Some applications of the method will be discussed, but not very many, because the applications of chromatography have already been treated thoroughly by others. Information and details of specific applications can be found in reference books[2,4] and reviews.[5]

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* There has been some suggestion from time to time that the term be used only when colored substances are being dealt with. Tswett named the method,[1] and was fully aware that it could be applied to colorless as well as colored substances. He distinguished *chromatography* from the more general term *adsorption analysis,* which subsumes not only chromatography but also capillary analysis. It seems reasonable to adhere to the well-nigh universal convention and keep the term chromatography whether or not the adsorptive is colored.

[1] Tswett, *Ber. deut. botan. Ges.,* 24, 316, 384 (1906).

[2] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography,* Wiley, New York, 1943; H. H. Strain, *Chromatographic Adsorption Analysis,* Interscience, New York, 1945. L. Zechmeister, *Progress in Chromatography 1938–1947,* Chapman & Hall, London, 1950.

[3] Zechmeister, *Ann. N. Y. Acad. Sci.,* 49, 145 (1948); *Isis,* 36, 108 (1945–6).

II. NATURE OF CHROMATOGRAPHY

Chromatography is essentially a method for *countercurrent application of adsorption.* In a simple case the adsorbent to be used is packed in a tube to form a *column* and the fluid to be analyzed is passed through it. Of course, here the column of adsorbent is held motionless and the fluid passes through it, but obviously relative to each other the fluid and adsorbent move in opposite directions. This fact explains the efficiency of the chromatographic method.[6] If it is recalled that adsorption is a distribution process (in which the adsorptive is distributed between a fluid and an interfacial phase) then it becomes clear that chromatography belongs with those other distribution processes, such as fractional distillation under reflux, countercurrent liquid–liquid, and other extractions,[7] which as separation processes owe their superiority over the related simple batchwise processes to their countercurrent natures (Chapter VI). Adsorption had early been used in what are now recognized as countercurrent operations: in sugar purification,[8] and in studies on the origin of

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[4] G. Hesse, *Adsorptionsmethoden im chemischen Laboratorium mit besonderer Berucksichtigung der chromatographischen Adsorptionsanalyse (Tswett-Analyse),* DeGruyter, Berlin, 1943. T. I. Williams, *An Introduction to Chromatography,* Blackie, London, 1946 (Chemical Pub. Co., Brooklyn). H. Willstaedt, *L'Analyse Chromatographique et Ses Applications,* Hermann, Paris, 1938. E. Lederer, *Progrès Récents de la Chromatographie, Première Partie, Chimie Organique et Biologique,* Hermann, Paris, 1949.

[5] Austin and Shipton, *J. Council Sci. Ind. Research,* 17, 115 (1944); Binkley and Wolfrom, *Scientific Report Series,* No. 10, Sugar Research Foundation, Inc., New York, 1948; Cassidy, *Proc. Pharm. Manuf. Assoc., Sci. and Med. Conferences,* 1949, p. 19; Meunier, *Chimie & industrie,* 52, 68 (1944); papers on chromatography, *Ann. N. Y. Acad. Sci.,* 49, 141–326 (1948); "Chromatographic Analysis," *Discussions Faraday Soc.,* No. 7 (1949); Strain, *Anal. Chem.,* 21, 72 (1949); *ibid.,* 22, 41 (1950).

[6] Cassidy, *J. Chem. Ed.,* 23, 427 (1946).

[7] Randall and Longtin, *Ind. Eng. Chem.,* 30, 1063 (1938).

[8] V. R. Deitz, *Bibliography on Solid Adsorbents.* J. M. Brown, Revere Sugar Refinery, Charlestown, Mass., 1944.

petroleums.[9] However, to Tswett belongs all the credit for the invention of chromatography and the recognition of its analytical value.[9]

The procedure of chromatography may be generalized as follows. The solution to be analyzed is passed through a column of adsorbent, whereupon any adsorbable materials present are brought into contact with the solid interface where they concentrate. The situation may be represented as shown below, with the understanding that equilibrium may not be reached:

$$\text{substances in solution} \rightleftharpoons \text{substances in interface}$$

In a simple case, where the solution contains a single solute and the adsorbent is efficient, the solute is adsorbed near the top of the adsorption column and there reaches a concentration which is in equilibrium, or nearly so, with the incoming solution. This comes about as a result of the flow of liquid. The first liquid, which meets the adsorbent, is depleted of solute when the adsorption occurs, and if this liquid were to remain in contact with the adsorbate (*i.e.*, if it did not move on) then the amount adsorbed would be conditioned by the concentration of the *depleted* solution, thus:

$$\text{depleted solution} \rightleftharpoons \text{substance adsorbed in interface}$$

However the depleted solution flows onward from this site and its place is taken by fresh solution of a higher concentration (*i.e.*, not yet depleted solution) so that further adsorption can and does occur. This process continues, the solution depleted by removal of substance to the interface being replaced by fresh solution until eventually the concentration of adsorbed substance on the adsorbent comes into equilibrium with the solution at its *original* concentration, thus:

$$\text{original solution} \rightleftharpoons \text{substance in interface}$$

But the depleted solution flows onward to fresh adsorbent, so that it eventually becomes wholly depleted of adsorbable solute, and the pure solvent flows on out of the bed of adsorbent. There is thus built up by this process a *zone* of adsorbed substances in the column. This can be observed visually if the substance is colored and the adsorbent is white or of a different color. It has the appearance of a band of color on the adsorbent, and is sometimes called a "band." But inasmuch as a band suggests a flat strip which has width but little depth, while examination of the zone shows, as would be expected, that the adsorption occurs throughout the section roughly bounded by this "band," it is preferable to use the term zone rather than band to describe this region of adsorption.

If two solutes are present in the solution, and one is more strongly adsorbed than the other, then the phenomenon that occurs is essentially that described above except that it is complicated by the superimposition, and perhaps interaction, of the processes for each solute. The solvent also must be considered, since it is adsorbed to some extent, but its effect is being taken as a constant factor here. If the two substances are of different colors, and adsorbed to nearly the same extent, then it will be observed that at first both are adsorbed in a mixed zone near the top of the column (Fig. VIII-1*b*). But as more liquid passes the zone, and it broadens out, there may be some evidence of a separation of the two substances: the less well-adsorbed one may begin to appear at the leading edge of the mixed zone. This comes about because in the competition for the interfacial surface, which is of relatively limited area, the more strongly adsorbed substance displaces the less strongly adsorbed one, and this latter can be effectively held only in a lower portion of the column where the more strongly adsorbed substance is absent or where it is so very dilute that its displacing effect is relatively unimportant.

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[9] Zechmeister, *Ann. N. Y. Acad. Sci.*, 49, 145 (1948).

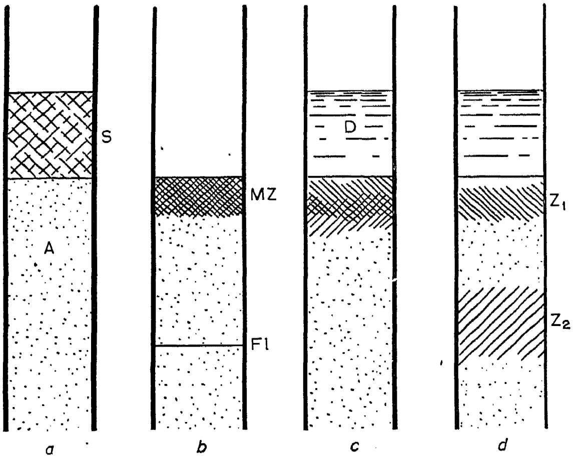

Fig. VIII-1. Chromatography of a binary mixture.
A, adsorbent as a column in a tube; S, solution of substances to be separated; Fl, front of empty solvent at the stage when the mixed zone MZ has just been formed; D, developer liquid; Z_1 and Z_2, zones of substances 1 and 2 from the mixture. (*a*) The solution has just been poured onto the column of adsorbent; (*b*) the solution has just all passed into the adsorbent, forming the mixed zone of adsorbate; developer is added at this point; (*c*) development is occurring and the zones of substances can be seen separating—empty liquid flows out at the bottom of the tube (not shown); (*d*) the chromatogram has been developed, and the two zones are seen to be well separated.

The first phase of the chromatographic analysis is completed when all of the substance has just passed into the adsorbent (Fig. VIII-1*b*). At this point it is said that the substances to be chromatographed have been *applied* to the column of adsorbent, and the initial *mixed zone* has been formed.

The object of the next phase of the process is to cause the adsorbed materials to become segregated on the adsorbent into individual zones, each of which, in favorable cases, is distinct from any other. This is accomplished by a process called *developing the chromatogram.* A liquid suitable as a developer liquid (it may be the original solvent, or a different one, or a mixture) is passed into the column *just* as the last part of the first solution enters (Fig. VIII-1*c*). This timing is important, for if air or other gas gets into the column it may cause channeling, and disrupt the zone. The "empty" developer liquid, coming into contact with the adsorbed material picks it up by a process of desorption, thereby depleting the adsorbent. As it moves over fresh adsorbate it picks up more and more solute until eventually, somewhere in the passage through the zone, the liquid may reach equilibrium with the adsorbate at a maximum concentration which is maintained almost to the leading edge of the zone. Here the concentration in the adsorbate decreases, and so deposition from the solution occurs and the liquid rapidly becomes depleted of solute. Thus the developer liquid, as Tswett puts it,[10] starts with zero concentration of solute, picks up substance in its passage through the zone until a maximum concentration is reached, then returns to zero concentration after depositing the substance in a lower portion of the column. This behavior causes the zone to migrate in the direction of flow of the liquid. It demonstrates very beautifully the operation of LeChatelier's principle. It should be pointed out that since this is a flowing system a condition of equilibrium may not be reached anywhere in the process. However an unsteady state approximating equilibrium conditions may be reached, depending upon various factors.[11,12] The rate at which the zone migrates is mediated by the rate of flow of the liquid as well as by the strength of adsorption of the substance involved. The more strongly adsorbed substance moves less rapidly than the one less strongly held, other conditions being equal, since it is less completely desorbed by the developer in its passage through the zone. This indeed is the basis of the sorting or separation process. For if the substances in the mixture are adsorbed with different degrees of tenacity then their zones will move at different rates under the influence of the flowing developer liquid, and hence if other conditions are favorable the zones draw away from each other and become completely segregated. At this stage the chromatogram is said to have been *developed,* or to have become developed.

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[10] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography,* Wiley, New York, 1943, p. 18.

[11] Thomas, *J. Am. Chem. Soc.,* 66, 1664 (1944); *Ann. N. Y. Acad. Sci.,* 49, 161 (1948).

[12] Walter, *J. Chem. Phys.,* 13, 229, 332 (1945).

It may happen, as Tswett pointed out,[13] that, during the development, less strongly held components may move sufficiently rapidly down the column that they pass completely out of it. In such a circumstance the substance from the zone may be collected as it emerges at the foot of the column, and several such zones, collected in succession, may be called, in Zechmeister's phrase, a *liquid chromatogram.* The process is *elution analysis.*[14]

Those zones which remain separated upon the column of adsorbent may now be recovered separately. The column is extruded from the tube and separated between the zones by cutting the column (with a spatula). The adsorbed substance in each zone is then recovered by *elution* or *desorption* with the aid of a suitable *eluent.* The most efficient elution with least solvent again makes use of the countercurrent arrangement; the adsorbent containing the zone is packed in a tube and the eluent solution is passed through it. Under favorable conditions the desired substance is desorbed and recovered quantitatively in the solution.

The process of chromatography has been described in a general way. Further brief remarks will be made concerning the nature of chromatography and then each factor in, and phase of, the process will be discussed in more detail.

Chromatography is not restricted to itemized applications but can be used wherever adsorption can be observed. The fluid in its passage through the adsorbent may move downward[13] or upward[15] or in any other direction, such as horizontally or radially[16] through a bed of adsorbent of whatever shape. Conversely, the adsorbent may be passed through the solution.[17] The movement may be produced under the pull of gravity, whether the liquid flows into the solid or the solid passes into the liquid. Vacuum may be applied to the adsorbent so that the fluid may be forced into it, or pressure may be applied to the fluid to force it into the adsorbent.[18] Centrifugation may be employed to force the liquid into the adsorbent or, presumably depending upon the arrangement, the adsorbent into the liquid.[19] The movement may be brought about by capillary forces,[20] or may be aided by some other agency.[21] In any case the adsorption process is carried out countercurrently, thus utilizing the capacity of the adsorbent to its fullest extent.

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[13] Tswett, *Ber. deut. botan. Ges.,* 24, 384 (1906).

[14] Tiselius, *The Svedberg* 1884–1944, Almqvist & Wiksells, Uppsala, 1944, p. 370.

[15] Tiselius, *Science,* 94, 145 (1941); Tiselius, in Kraemer, ed., *Advances in Colloid Science,* Vol. I, Interscience, New York, 1942, p. 81.

[16] W. G. Brown, *Nature,* 143, 377 (1939); Lapp and Erali, *Bull. sci. pharmacol.,* 47, 49 (1940); *Chem. Abstracts,* 34, 5776 (1940); Crowe, *Ind. Eng. Chem., Anal. Ed.,* 13, 845 (1941); Crowe and A. Walker, *J. Optical Soc. Am.,* 34, 135 (1944); Hopf, *Ind. Eng. Chem.,* 39, 938 (1947).

[17] Lowman, *Science,* 96, 211 (1942).

III. THEORY OF CHROMATOGRAPHY

Ideally, a theory of chromatography should describe in quantitative terms the course of the process: the formation and development of zones, their rate of movement, and their spatial as well as their concentration dimensions. It should make it possible to calculate beforehand, for example the state of development after a given amount of developer has been applied to the column. It should clarify the findings of experiment and should lead to predictions of possible new methods or observations. Not all of these ideals have been achieved, but considerable progress has already been made toward them.[22] Some of the features of chromatographic theory will be presented below, but if a thorough treatment of it is desired it must be sought in the original literature. The complications of the theory together with its present lack of practical usefulness preclude extensive discussion here. Instead, a qualitative treatment will be given, and only such quantitative aspects will be introduced as will be useful in later discussion of zone formation, etc.

In ordinary, batchwise adsorption operations, a quantity of adsorbent, m, is mixed with a quantity of solution, v, of concentration c_0. The process of adsorption which takes place serves to deplete the solution, so that its concentration falls to a new value, c. The amount of substance adsorbed is the amount which has disappeared from solution: $(c_0 - c)\,v$. The process may be allowed to reach equilibrium, in which case the amount of substance adsorbed, q, has a maximum value and may be related (at a given temperature) to the equilibrium concentration $c_{equil.}$ by means of the adsorption isotherm $q = mf(c_{equil.})$. The isotherm has been discussed in previous chapters. The important point here is that the adsorbed substance comes into equilibrium with a solution which has a concentration less than that of the original solution, since the act of adsorption depleted the solution. It is apparent, from an examination of an isotherm, that fewer molecules will be adsorbed at a concentration c (q mole/g. will be adsorbed at equilibrium) than could be adsorbed if the equilibrium concentration were higher, say c_0, where q_0 would be adsorbed (Fig. VIII-2).

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[18] Tswett, *Ber. deut. botan. Gest.*, 24, 316, 384 (1906).

[19] T. I. Williams, *An Introduction to Chromatography*, Chemical Pub. Co., Brooklyn, 1946; Hopf, *Ind. Eng. Chem.*, 39, 938 (1947).

[20] Flood *Tids. Kjemi, Bergvehen*, 17, 178 (1937); *Chem. Abstracts*, 32, 6575 (1938); *Z. anal. chem.*, 120, 327 (1940).

[21] Strain, *J. Am. Chem. Soc.*, 61, 1292 (1939).

[22] The literature is extensive, and is listed by Thomas, *Ann. N. Y. Acad. Sci.*, 49, 161 (1948). See also Klotz, *Chem. Revs.*, 39, 241 (1946); Claesson, *Arkiv Kemi, Mineral. Geol.*, A23, No. 1 (1946); Sillén, *ibid.*, A22, No. 15 (1946); Strain, *Anal. Chem.*, 21, 75 (1949); 22, 41 (1950); Harris, *Ind. Eng. Chem.*, 42, 20 (1950).

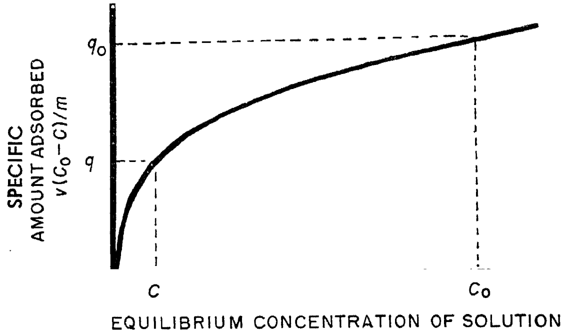

Fig. VIII-2. Adsorption isotherm for a substance which obeys the Freundlich relation $v(c_0 - c)/m = Kc^n$. Here v = volume of solution of concentration c_0, which is treated with a mass m of adsorbent. The equilibrium concentration is c. K and n are constants. The specific amount of substance adsorbed is q; then $q = Kc^n$.

The batch operation is completed by separating the solid and liquid phases. The solid carries with it the adsorbed molecules and some solvent. The adsorbed molecules can be recovered by elution.

Sanders[23] improved the efficiency of the simple batchwise adsorption operation by an *explicit* application to it of the principle of countercurrent action, which has since been widely used.[24] Sanders was interested in decolorizing sugar solutions. In this operation it was sufficient to reduce the "color" from an original value c_0 to a definite, low value c. The adsorption isotherm for the colored material (the "color") was described quite well by the Freundlich isotherm, which could be written in the form:

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[23] Sanders, *Ind. Eng. Chem.*, 20, 791 (1928).

[24] Hassler and Hagberg, *Oil & Soap*, 16, 188 (1939); Kearby, U. S. Pat. 2,384,311 (Sept. 4, 1945); *Chem. Abstracts*, 40, 343 (1946); Berg, *Trans. Am. Inst. Chem. Eng.*, 42, 665 (1946); Hopf, *Ind. Eng. Chem.*, 39, 938 (1947); Stenerson, *Chem. Eng. News.*, 25, 1768 (1947); Peck, *Ann. N. Y. Acad. Sci.*, 49, 235 (1948); Kehde, Fairfield, Frank, and Zahnstecher, *Chem. Eng. Progess*, 44, 575 (1948); R. Williams, Jr., and Hightower, *Chem. Eng.* (Nov., 1948).

$$v(c_0 - c)/m = Kc^n$$

Here $v(c_0 - c)$ is the amount of color removed by m grams of decolorizing charcoal, and K and n are constants. It is possible to calculate, on the basis of the isotherm, how much charcoal would be needed in a given volume of solution to reduce the color from c_0 to c in one-step, two-step, or three-step, etc. operations. The operation considered is such that fresh adsorbent enters the system and comes into contact first with partly decolorized liquid, reducing its concentration to the final low value c. The partly spent charcoal is then used stepwise against progressively less decolorized liquids until it emerges from the system as completey spent as possible. The operation for a three-stage system is illustrated in Figure VIII-3. The calculations for Sanders' method are not given. The results

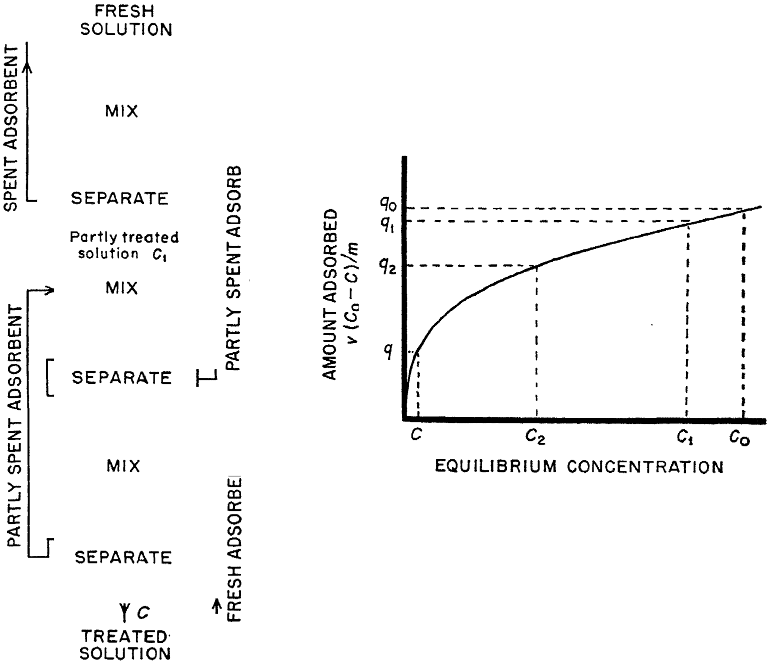

Fig. VIII-3. Cascade application of adsorption.
The isotherm is shown, together with a flow diagram of the operations for a three-stage process. The spent adsorbent leaves the system with a concentration of c_1 after having adsorbed an amount q_1 of adsorptive per gram. The treated solution leaves at concentration c having been brought to this value by fresh adsorbent.

of the calculations for a particular isotherm are gathered into Table VIII-1. It should be mentioned that in starting such a system as this the initial batch of charcoal is not used in a countercurrent way. The calculations are for a system which is already *in operation.*

When the three-stage system is in operation (Fig. VIII-3), fresh adsorbent of quantity 0.366 m (in the case illustrated) enters the system first into contact with liquid of concenration c_2 (*i.e.,* liquid which is already partially decolorized). This fresh adsorbent is in sufficient quantity to lower the concentration of the solution to an equilibrium value c, at which point the amount of color adsorbed on the charcoal is $(c_2 - c)v$. The adsorbent is separated from the solution and brought next into contact with liquid of concentration c_1, from which it adsorbs a quantity $(c_1 - c_2)v$ of color and brings this solution to an equilibrium concentration of c_2, itself having a total quantity q_2 of solute adsorbed upon it. The mixture is then separated, and the solution of concentration c_2 passes on to meet a fresh batch of adsorbent. The partly used adsorbent is next brought into admixture with the fresh solution of concentration c_o and is able to bring its concentration to c_1 by adsorbing $(c_o - c_1)v$ of color. The adsorbent then leaves the system in equilibrium with solution of concentration c_1 and carrying adsorbed upon it q_1 of solute.

TABLE VIII-1

Comparison of Single-Stage and Multiple-Stage Use of an Adsorbent

The isotherm is $v(c_0 - c)/m = 1.2c^{0.32}$

Operation	Amount of adsorbent used, g.
One-stage	m
Two-stage	0.436 m
Three-stage	0.366 m
Four-stage	0.347 m

When the three-stage is compared with the single-stage operation it becomes evident why less adsorbent is needed in it, for in the case of the three-stage operation the adsorbent leaves the system in equilibrium with a solution of the relatively high concentration c_1, whereas in the single-stage operation it leaves at a concentration of c. Thus, mass for mass, the adsorbent removes more solute in the former than in the latter case, and hence to remove a given amount of solute less adsorbent is used in the former than in the latter. The calculation involves figuring the amount of adsorbent needed so that:[25]

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[25] For a discussion and aids to computation, see *Handbook for Counter-current Treatment with Activated Carbon,* Darco Corp., New York.

$$(c_o - c_1)v = q_1 - q_2; \quad (c_1 - c_2)v = q_2 - q; \quad (c_2 - c)v = q;$$
$$(c_o - c)v = q$$

The discussion and the table show that, after the system is in operation, the greater the number of stages in which the adsorbent can be applied the less is the amount of charcoal needed to produce a given decolorization. Sanders showed also that the greater the percentage of substance which is to be removed, that is, the further toward zero is to be the final concentration c, the more efficient is the countercurrent compared with the single-stage operation. This work establishes two points: first, that in the countercurrent application less adsorbent is required to remove a given amount of solute than in a single-batch operation, and, second, that the more complete is to be the removal of solute the more efficient is the countercurrent operation over the single-stage operation. The qualitative application of these two points to chromatography resides in this, that the substance adsorbed in a zone is *completely* removed from the solution applied to the column, and that the chromatographic process, being truly countercurrent in nature, causes the initial zone (in the limit of equilibrium) to be built upon the smallest possible amount of adsorbent consistent with the initial concentration of the solution. The action of solution and adsorbent in a Tswett column may be looked upon as a repetition and integration of a very large number of very small stages in a countercurrent manner.

It is theoretically almost impossible to remove all of the solute in a single-batch adsorption because no matter how much adsorbent is used the liquid in equilibrium with it, according to the laws of distribution. will still retain some solute. This makes the Sanders method of calculation inapplicable to chromatography. The reason that the substance adsorbed in the zone is completely removed from solution follows from Wilson's explanation of why the leading edge of the zone is sharp[26] with isotherms of the shape shown (see below). Wilson points out that an infinitesimal element of solution passing over an infinitesimal element of length of column just beyond the leading edge of the zone deposits an infinitesimal amount of adsorptive, but the concentration of this element of volume decreases by a finite amount, so that the concentration of the solution becomes zero within an infinitesimal distance of the leading edge of the zone.

The theory of chromatography first developed by Wilson[26] and later extended by DeVault,[27] Weiss[28] and others (see above), leads to the following general equation for the chromatography of a single solute:

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[26] Wilson, *J. Am. Chem. Soc.*, 62, 1583 (1940).

[27] DeVault, *J. Am. Chem. Soc.*, 65, 532 (1943).

[28] Weiss, *J. Chem. Soc.*, 1943, 297.

$$\partial c/\partial x + [\alpha + Mf'(c)]\partial c/\partial V = 0$$

In this equation c = the amount of solute in solution per unit volume of solution; x = the distance down the column (from the top) of a point under consideration; α = the interstitial volume per unit length of column, that is, the accessible space filled with solution between and in the particles of adsorbent; M = the amount of adsorbing material per unit length of column; V = the volume of liquid which has passed into the column (initially filled with liquid) between an initial time and the time in question (V may serve as a measure of time); and f' = the first derivative of the function f in the adsorption equation (see below).

The equation states that the amount of solute removed from an infinitesmal volume of solution as it passes over an extremely thin cross section of adsorbent is equal to the amount of solute deposited on this section of adsorbent; that is, the change in concentration in the solution and the change in concentration in the interface fully account for the solute present. The amount of solute, Q, adsorbed per unit length of column is related to the concentration of solute in equilibrium with it by the isotherm equation $Q = Mf(c)$. The equation of chromatography makes it possible to calculate the distribution of adsorbed material in the column after a volume of solution containing adsorbable substance has passed through it. In deriving this equation it is assumed that equilibrium between solution and adsorbate is reached instantaneously. The effect of diffusion is neglected and the packing of the column is taken to be uniform.

The general solution of this general equation is written by DeVault as:

$$c = \phi(V - x[\alpha + Mf'(c)])$$

Here ϕ is an arbitrary function determined partly by the initial conditions of the chromatography, *i.e.*, whether the column initially contains no adsorbed substance or contains a certain distribution of adsorbed substance in equilibrium with adjacent solution. The equations for the boundaries of a zone are derived from the general equations by the application of boundary conditions and the requirement of the conservation of matter.

According to the theory when the solution to be chromatographed is applied to an "empty" column, that is, one containing no adsorbed substance except, perhaps, solvent, the zone which is first formed has a uniform concentration, the amount of substance adsorbed per unit length of column being $Q_0 = Mf(c_0)$ (see Fig. VIII-4). When developer liquid passes into the column the zone begins to move downward as substance is desorbed from the trailing face of the zone (the top part, if the liquid is flowing downward through the column). The "empty" developer liquid picks up this substance, carries it down, and deposits it at the leading face of the zone at which the substance-bearing developer encounters "empty" adsorbent. At the same time the zone broadens out, the way in which it behaves being a function of the type of isotherm given by the substance.

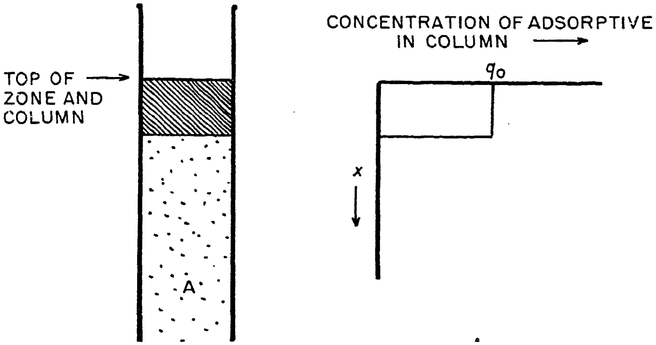

Fig. VIII-4. Theoretical profile of a zone. The zone is shown on the column at the left, and its concentration profile is plotted at the right.
A is the adsorbent in the column; q is the amount of material adsorbed per gram; x is the distance down the column. This shape of profile is often quite closely approached when the adsorptive has been just applied to the column, and before development has been begun.

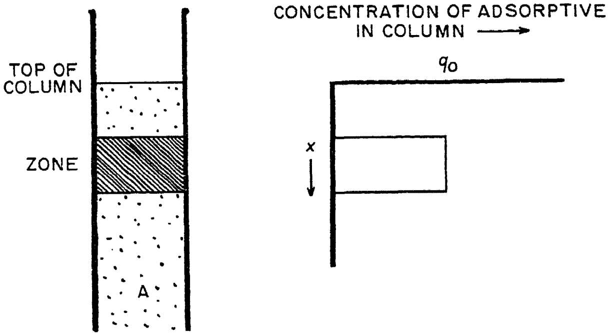

Fig. VIII-5. Theoretical development of the zone shown in Figure VIII-4 for the case of a linear isotherm.

If the isotherm is linear, with a finite slope, then the zone would be expected to move down the column, at the same time remaining sharp on both faces except as diffusion, channeling, etc. might diminish the sharpness (Fig. VIII-5). This was predicted by the Wilson theory and that of Martin and Synge.[29] Linear adsorption isotherms with finite slopes are not often encountered, except in certain cases of very dilute solutions so that this behavior of the zone is not typical of chromatography.

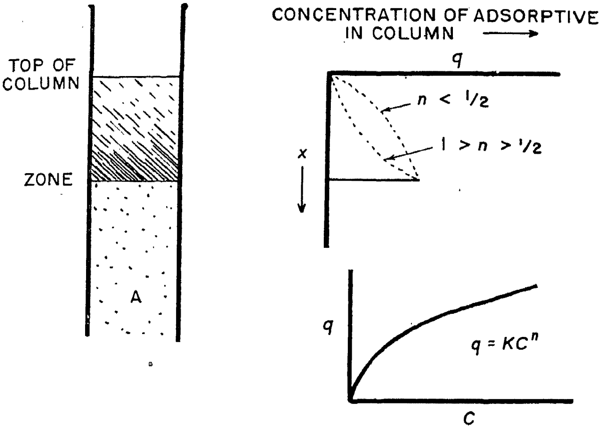

Fig. VIII-6. Development of a zone for the case of an isotherm of the shape shown in the lower right. C is the equilibrium concentration; K and n are constants. Other symbols are the same as in Figure 4.

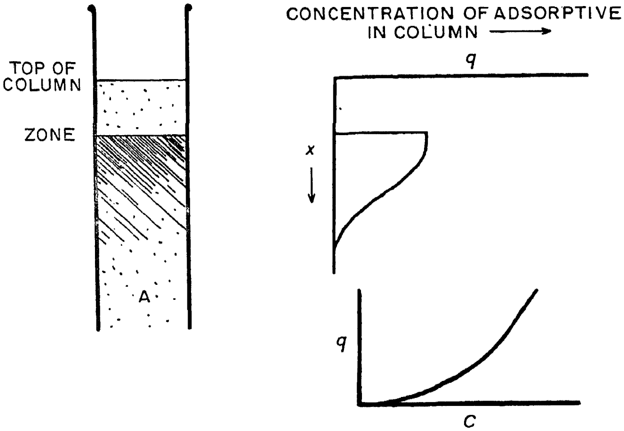

Fig. VIII-7. Profile of a zone in development when the isotherm is of the shape shown in the lower right.

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[29] Martin and Synge, *Biochem. J.*, 35, 1358 (1941).

In the experiments of Martin and Synge the effective partition (liquid–liquid) does sometimes appear to have a linear isotherm over a considerable range of concentration. This behavior is also mentioned by Tiselius.[30]

Most adsorption isotherms for solutions and solid adsorbents exhibit a curve of the type shown in Figure VIII-3. In this type of isotherm, $Q = Mf(c)$, f' is a decreasing function of c, and $f''(c)$ is negative, *i.e.*, if the isotherm is $q = Kmc^n$ then the exponent is a positive number less than 1. (If $n = 1$ then we have a linear isotherm, in which case f' is a constant and $f''(c)$ is zero.) In such cases the theory predicts that the leading face of the zone should remain sharp, and the following face should be diffuse, should "tail off," the concentration profile of the "tail" depending upon the shape of the isotherm (Fig. VIII-6).[31,32]

If the situation exists where the adsorption isotherm has the shape shown in Figure VIII-7, then it would be expected that the front of the zone would show a certain diffuseness.[31] This would occur also if at the front of the zone equilibrium were not fully established, even though the isotherm were linear.[32]

This discussion so far has been predicated upon close approach to equilibrium with pure adsorptives. A small amount of impurity running just ahead or just behind a zone could simulate a diffuse front or trailing boundary.

During the process of development, then, for all except linear isotherms, the zone broadens and eventually the portion of original concentration q_0 disappears. This is the condition at which Weiss[32] and Weil-Malherbe[33] define the zone to be fully developed. They give methods for calculating the minimum volume of liquid required to produce this "full development" and for calculating the maximum concentration of solution in equilibrium with the front face of a fully developed zone. If this zone is eventually washed out of the column then a useful quantity can be defined, the "threshold volume" V_t. This is the volume of liquid which passes out at the base of the column up to the appearance of the leading face of the zone of which it is the threshold volume.[33] This volume of liquid is made up of the liquid in which the substance to be adsorbed was dissolved (volume v_0) plus additional developer liquid (v_t, the "threshold" volume of Weiss[32]). If the column was already wet with a volume of liquid v_α, then this liquid also appears, and the measured volume V, collected at the base of the column up to the point when the zone appears, consists of $V_t + va$. That is, this threshold volume is measured for a dry column or is calculated to a dry column. This threshold volume obviously depends upon the amount of adsorbent in the column.

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[30] Tiselius, *Arkiv Kemi, Mineral. Geol.*, **A16**, No. 18 (1943).

[31] DeVault, *J. Am. Chem. Soc.*, **65**, 532 (1943).

[32] Weiss, *J. Chem. Soc.*, **1943**, 297.

[33] Weil-Malherbe, *J. Chem. Soc.*, **1943**, 303.

DeVault tested the theory of chromatography against data obtained by Cassidy and Wood[34] and found reasonably good fit between the two. (Fig. VIII-8). A few comments may be made about this figure. In it the point V_{x_d} represents the volume of liquid that must pass the bottom of the column (which is x_d from the top) before the leading boundary of the zone leaves the bottom of the column. In the experiments of Cassidy and Wood a column of dry charcoal was treated with a volume of solution which contained more solute than was needed to totally "saturate" the adsorbent at that concentration so that at the moment when the sharp leading boundary had passed the bottom of the column and solution of concentration c_0 was emerging, solution of concentration c_0 was still passing into the top of the column. The entire column was in equilibrium, or nearly so, with the liquid of initial concentration c_0 and the amount of substance adsorbed could be calculated from the static, equilibrium isotherm. The calculated value checked reasonably well with the amount of soute removed from the percolate up to the point where its concentration became c_0. (The arrangement is like that of frontal analysis.)

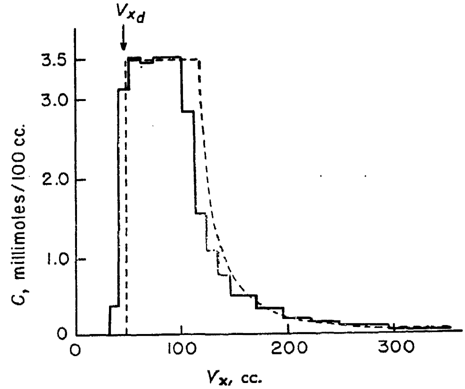

Fig. VIII-8. Test of the DeVault theory. The solid line is the plot of the experimental data and the broken line, of the theory[31]

The less than perfect fit between theory and data is laid by DeVault to possible error in the empirical expression for the isotherm as determined by Cassidy and Wood, and the lack of sharpness of the front boundary to possible channeling of the column. (See, however, the discussion of the shapes of zone faces, above.) Some of the diffuseness of the leading face of the zone in the experiments of Cassidy and Wood may have been the result of the arrangement of the apparatus. The column was supported on a pad of cotton, and this retained some fluid so that a certain mixing and dilution of the first small amount of solute to leave the column occurred in this volume of solution. However, the fairly large fractions in which the percolate was collected probably minimized this effect. DeVault suggests that the adsorption isotherm might be obtained from the shape of the following (rear) boundary of the zone in favorable cases, using the equation $f'(c) = V_x/Mx$. Here V_x/Mx would be determined experimentally as a function of c to obtain f. The sharp leading boundary where $V_{x_d}/Mx = f(c_o)/(c_o)$ might serve to check the integration or to yield a constant of integration.

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[34] Cassidy and Wood, *J. Am. Chem. Soc.*, 63, 2628 (1941).

The discussion so far has applied to a single-solute chromatography. In the case of multiple solutes the equations which apply are a set of simultaneous partial differential equations of the type;

$$\partial c_i/\partial x + \alpha\, \partial c_i/\partial V + \partial Q_i/\partial V = 0$$

where, for example, Q_i is the amount of the ith solute adsorbed per unit length of column in equilibrium with the concentration c_i of this solute, there being n solutes present. It is not profitable here to go into a discussion of this case, since little is known about the effects of the presence of other solutes on the adsorption of one solute. That is, little is known about relations of the type:

$$Q_i = Mf_i\ (c_1,\ c_2 \ldots c_i \ldots c_n)$$

Further complication is introduced by the fact that the concentrations may all be changing simultaneously.

It seems that at present, in spite of the use of plausible assumptions, the theory of chromatography cannot be applied usefully to the case of multiple solutes, although progress is being made in that direction.[35] A kinetic approach was made to the problem by Thomas[36] in connection with exchange reactions, and later Walter[37] independently confirmed Thomas' conclusions. Thomas reported, also, a test of the theory.[38] The problem has been attacked also by others in connection with the chromatography of ions on exchangers.[39]

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[35] Offord and Weiss, *Nature*, 155, 725 (1945); 156, 570 (1945); Glückauf, *ibid.*, 156, 205 (1945); *Proc. Roy Soc. London*, A186, 35 (1946); *J. Chem. Soc.*, 1947, 1321; Nestler and Cassidy, *J. Am. Chem. Soc.*, 72, 680 (1950).

[36] Thomas, *J. Am. Chem. Soc.*, 66, 1664 (1944).

[37] Walter, *J. Chem. Phys.*, 13, 229, 332 (1945).

[38] Thomas, *Ann. N. Y. Acad. Sci.*, 49, 161 (1948).

Tiselius[40] has approached the problem in a fruitful way. By imposing certain arbitrary limitations on the carrying out of the chromatography he has achieved a simplification of the theory together with important practical advantages in the operation of the method. One of the simplifications which he uses is to employ a short column and more than enough solution of original concentration c_o to saturate the column with adsorbable substance (frontal analysis). Figure VIII-9 shows the progress of the analysis of a solution containing a single solute. The solution of concentration c_o is passed up through a short column containing m grams of adsorbent and, initially, no solution or adsorbed substance. The solute

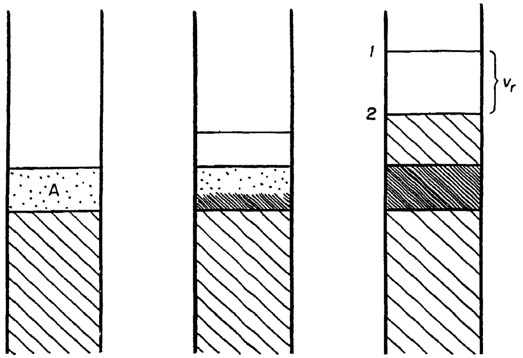

Fig. VIII-9. Frontal analysis of a solution containing a single adsorptive. (*a*) The solution is about to pass upward into the short column of adsorbent, A; (*b*) the adsorbent is partly saturated with adsorptive and empty solvent has emerged above the column of adsorbent; (*c*) the solution has passed on through the saturated column. Fronts, where refractive index undergoes a sharp change are seen at *1* (empty solvent–air front) and *2* (original solution–empty solvent front). v_r is the retention volume—in this case the volume of empty solvent.

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[39] See, for example, Boyd, Schubert, and Adamson, *J. Am. Chem., Soc.*, 69, 2818 (1947); Boyd, Adamson, and Myers, *ibid.*, 69, 2836 (1947); Boyd, Myers, and Adamson, *ibid.*, 69, 2849 (1947); Mayer and Tompkins, *ibid.*, 69, 2866 (1947); Tompkins, Khym, and Cohn, *ibid.*, 69, 2769 (1947).

[40] Tiselius, *Arkiv Kemi, Mineral. Geol.*, **B14**, No. 22 (1940); **B14**, No. 32 (1941); **B15**, No. 6 (1941); *Science*, 94, 145 (1941); *Arkiv Kemi, Mineral. Geol.*, **A16**, No. 18 (1943); Tiselius and Claesson, *ibid.*, **B15**, No. 18 (1942); Tiselius, *Kolloid-Z.*, 105, 101 (1943); Tiselius and Hahn, *ibid.*, 105, 177 (1943); Tiselius, in Kraemer, ed., *Advances in Colloid Science*, Vol. I, Interscience, New York, 1942, p. 81.

is adsorbed, as the zone is built up, in the manner discussed previously (see Fig. VIII-4). In Figure VIII-9*a*, the solution is about to enter the adsorbent; in VIII-9*b*, the adsorbent is partly filled and "empty" liquid is emerging above the column. In Figure VIII-9*c*, the leading face of the zone has reached beyond the top of the column and liquid of concentration, c_0, has passed out of the column. The volume of liquid which has emerged from the column to the point where the solute appears is named the *retention volume,* v_r. It is equivalent to the quantity V_{x_d} in Figure VIII-8. If the retention volume is divided by the mass of the adsorbent in the column then the *specific retention volume,* v_r, is obtained. It is equivalent to V_{x_d}/Mx_d in the experiment of Cassidy and Wood. If the column initially contained solvent, then this solvent, of volume v_α will be displaced by the entering solution and the observed volume of liquid V up to the point where solute appears at the foot of the column will be $v_r + v_\alpha$. The retention volume of Tiselius is not necessarily the same as the threshold volume of Weil-Malherbe,[17] since the former does not allow for any development of the zone while the latter implies at least some development.

Further simplification is achieved by Tiselius by considering only one initial concentration of the substance in question. Thus, if the substance A has an initial concentration in the solution c_A ($= c_0$ for substance A) then the emerging liquid will be at a concentration c_A. There is no concentration gradient in the adsorbent. The amount of substance adsorbed will equal that removed from the retardation volume, or $c_A v_r$. But *at this concentration* the amount of substance adsorbed per unit mass of adsorbent can be related to the equilibrium concentration c_A by an "adsorption coefficient" α_A, so that $q_A/m = \alpha_A c_A$ and $\alpha_A c_A m = c_A v_r$. Also $v_r/m = v_r = \alpha_A$. The adsorption coefficient is dependent on the concentration (for ordinary, nonlinear isotherms), as will the specific retardation volume be also. But by defining conditions sufficiently there can be prepared tables showing specific retardation volumes of different substances (in cubic centimeters) for solutions of definite concentration on a given adsorbent (Table VIII-2). Tables showing specific retardation volumes of fatty acids, amino acids, peptides, saccharides, and other substances may be found in Tiselius' papers referred to above.

If two adsorbable substances, A and B, are present, then two "fronts" will appear as shown schematically in Figure VIII-10. The first front will be that of the less strongly adsorbed substance, A, and the next that of the mixture, $A + B$. If the two substances do not influence the adsorptions of each other, as they may not in very dilute solutions, then it will be as though the separate behaviors were superimposed. However, ex-

TABLE VIII-2

Specific Retention Volumes in Cubic Centimeters per Gram of "Carbo Active" for Acids in 0.5% Aqueous Solutions (after Tiselius)

Acetic acid	5.5
Propionic acid	7.6
Butyric acid	11.0
Succinic acid	13.0
Tartaric acid (racemic)	11.4
Tartaric acid (meso)	7.0

cept in the most dilute solutions the components influence the adsorptions of each other and Tiselius has found that the displacing effect of the more strongly adsorbed *B* causes the concentration of *A* in the "front" of *A* to be higher than it was in the original solution, *i.e.*, higher than c_A.

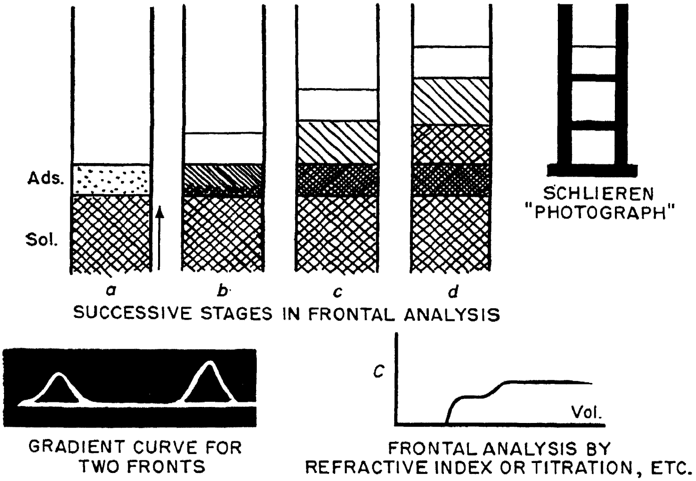
Ads.
Sol.
a
b
c
d
SCHLIEREN "PHOTOGRAPH"
SUCCESSIVE STAGES IN FRONTAL ANALYSIS
C
Vol.
GRADIENT CURVE FOR TWO FRONTS
FRONTAL ANALYSIS BY REFRACTIVE INDEX OR TITRATION, ETC.

Fig. VIII-10. Successive stages in the frontal analysis of a binary mixture (after Tiselius). (*a*) The solution of substances *A* and *B* is about to enter the adsorbent, Ads.; (*b*) the adsorbent is saturated with substance *A*, and partly with *B*; (*c*) the front of *A* has appeared with empty solvent (retention volume of *A*) above it, and the adsorbent is shown just saturated with *A* and *B*; the front of $A + B$ is about to appear; (*d*) the fronts of *A* and $A + B$ have appeared. The retention volume of *B* is the entire volume above the front of $A + B$. A schlieren photograph is shown diagrammatically at the right for these fronts. Below are gradient curves showing regions at two fronts where refractive index *changes* sharply. A frontal analysis diagram is shown at the lower right, where *C* is concentration determined by any means. The distance up to the first "step" is a measure of the retention volume for *A*, and up to the second step for *B*.

At the second "front" the total concentration is that of the original solution. Claesson[41] has given a clear discussion of frontal analysis, together with the calculations by means of which in favorable cases the concentration of each component of a mixture may be determined. Some of his experimental data are gathered in Table VIII-3. For the analysis of the first mixture in the table about 0.2 g. was used.

The analytical usefulness of the method resides in its ability to indicate the number of components in a mixture by the number of the fronts which appear; the nature of each component approximately by its retardation volume; and the concentration of the component by the concentration difference at the front (taking into account previous fronts[41]). The mutual influences of components that tend to alter the individual retardation volumes and to introduce error into the calculation of initial concentrations impair the usefulness of the method.

TABLE VIII-3

Frontal Analyses[41] of Synthetic Mixtures of Fatty Acids, from Absolute Alcohol onto Carboraffin CIV

Mixture of fatty acids	Concentration	
	As made up, %	In relative percent as found
Octanoic	20	21
Decanoic	20	19
Tetradecanoic	20	20
Hexadecanoic	40	41
Octanoic	20	21
Decanoic	20	16
Tetradecanoic	20	20
Hexadecanoic	40	44
Octanoic	10	14
Nonanoic	10	10
Decanoic	10	8
Dodecanoic	20	22
Tetradecanoic	20	20
Hexadecanoic	30	27

IV. APPARATUS AND MATERIALS

The whole chromatographic process will now be examined in some detail from the practical, manipulative point of view. Besides the mixture to be separated or analyzed there is needed suitable apparatus and a suitable solvent, adsorbent, developer, and eluent. The solvent, developer, and eluent are often distinuished only for convenience; the solvent is the liquid used to bring the mixture onto the column; it may also be used as the developer by means of which the zones are sorted apart into the developed chromatogram. The eluent is only a more powerful developer. These apparatus and materials will be discussed first; then the process itself will be treated from the standpoints of the manipulations involved in the chromatography and the phenomena which accompany them.

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[41] Claesson, *Arkiv Kemi, Mineral. Geol.*, A23, No. 1 (1946).

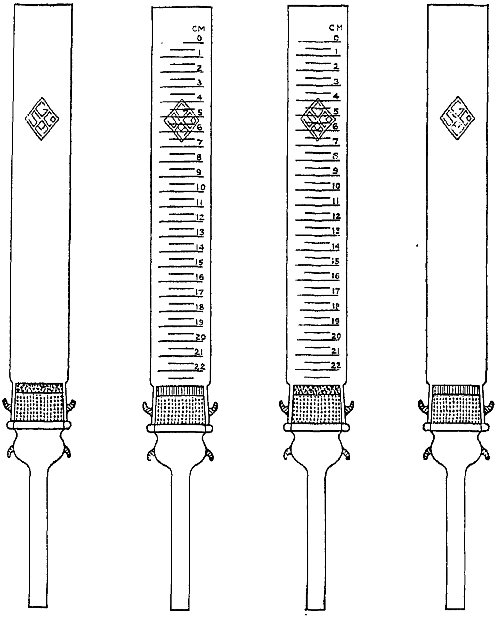

Fig. VIII-11. Chromatography tubes (Courtesy Scientific Glass Apparatus Co., Inc.)

The *apparatus* needed for chromatography can usually be of the simplest kind: a tube in which the adsorbent can be retained in the form of a column; containers for the original solution and the fractions obtained from the column; perhaps several smaller tubes for use in eluting zones; and perhaps a dowel for packing the adsorbent into the column.

The column of adsorbent must be given support in the tube, and this can be done in any reasonable way. If the tube is a narrow one an indentation or constriction supporting a wad of cotton or glass wool is sufficient, and the column is formed upon this. If the tube is wider, the cotton may be supported upon a perforated porcelain plate or a fritted glass plate which rests on the indentation. As an alternative, a perforated cork may be thrust into the bottom of the tube and the cotton wad placed on it. The tube itself may be of any cross-sectional shape: circular is usual for obvious reasons; square has been suggested for special purposes.[42,43] The tube may be of glass, quartz,[42] "plastic" such as Lucite,[44] cellophane or similar material,[45] or metal.[44] It may be constructed so that it can be opened longitudinally[44] or laterally.[43] It is convenient but not necessary to have the tube long enough so that there is a space above the column for a supply of liquid, whether of original solution or of developer (Fig. VIII-11). A bulb may be made in the upper part of the tube. This arrangement has certain advantages: the bulb serves as a liquid and pressure-space reservoir, thus shortening the over-all length needed; its presence need cause no inconvenience in extruding the column provided that the neck of the bulb has a wider opening than the column itself. A piece of paper is rolled into a tube to form a removable lining and inserted down to the stem of the bulb. The column is then extruded into this paper tube, which is withdrawn and unrolled to expose the column. In making up these tubes the internal diameter of the glass tubes should be measured. If they show a taper, as they sometimes do, the tapered tubes should be used with the narrower end at the bottom of the apparatus. Tubes specially prepared with a slight taper to aid extrusion of the column of adsorbent have been designed.[46]

Chromatography does not necessarily require a tube. The adsorbent may be spread on an inclined surface in the form of a flat strip[47] or a half-disk[48] (Fig. VIII-12), the solution being applied at one end or at the middle of the straight side, in the one and the other case. The adsorbent may be supported in paper by precipitating it within the pores,[49] or blotting or filter paper may be used between glass plates[50] (Fig. VIII-13), or a film of powdered adsorbent may be layered between the sheets of paper.[50] The adsorbent in the form of folded strips, disks of paper, or cloth may be piled up in a tube,[51] or clamped without the use of a tube.[49] It is evident that great versatility in arrangement is possible, and that much ingenuity has been applied to devising apparatus for chromatography. One can, however, almost always use simple apparatus which one has at hand in the laboratory. Some of the devices referred

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[42] Karrer and Schöpp, *Helv. Chim. Acta,* 17, 693 (1934).

[43] Békésy, *Biochem. Z.,* 312, 100 (1942).

[44] Crowell and König, *Ind. Eng. Chem., Anal. Ed.,* 16, 347 (1944).

[45] Otiai and Takeuti, *J. Pharm. Soc. Japan,* 58, 724 (1938); *Chem. Abstracts,* 33, 504 (1939).

[46] Georges, Bower, and Wolfrom, *J. Am. Chem. Soc.,* 68, 2169 (1946).

[47] Lapp and Erali, *Bull. sci. pharmacol.,* 47, 49 (1940); *Chem. Abstracts,* 34, 5776 (1940).

[48] Crowe, *Ind. Eng. Chem., Anal. Ed.,* 13, 845 (1941).

[49] Flood, *Tids. Kjemi, Bergvesen,* 17, 178 (1937); *Chem. Abstracts,* 32, 6575 (1938); *Z. anal. Chem.,* 120, 327 (1940); Mitchell and Haskins, *Science,* 110, 278 (1949). Carl Schleicher and Schuell Co. advertise papers impregnated with infusorial earth, and with charcoal.

[50] Brown, *Nature,* 143, 377 (1939).

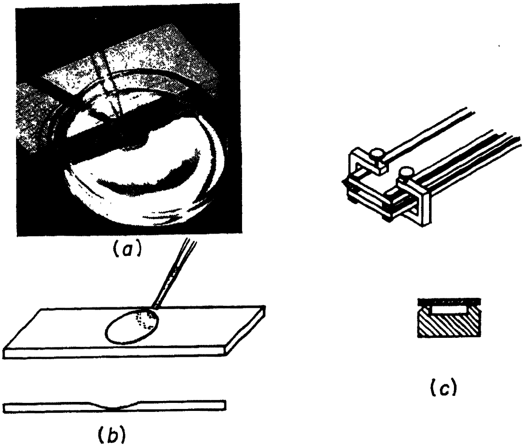

Fig. VIII-12. Apparatus for chromatography on a small scale, using strips or wedges of adsorbent. (*a*) A wedge of adsorbent is formed in a petri dish; the substance to be separated is applied in the center of the straight edge[48]; (*b*) the adsorbent is placed in the ground depression in a "hanging drop" microscope slide; (*c*) the column is formed between two glass plates separated by spacers, or in a covered trough.[48]

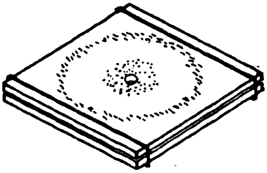

Fig. VIII-13. Chromatography with filter paper.[50] The sheet of filter paper or a layer of adsorbent is placed between glass plates to suppress evaporation of solvent. The substance to be chromatographed is introduced through the hole in the center of the upper plate, and followed with developer.

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[51] Lenoir, *Bull. soc. chim.*, **9**, 475 (1942); Mitchell and Haskins, *Science*, **110**, 278 (1949).

to above, such as those using paper, are able to handle only small amounts of material. On the other hand, adsorption columns are used also for handling quite large quantities of adsorptives.[52]

The *choice of size of tube* for containing the adsorption column depends primarily upon the amount of adsorbent which is to be used, and this depends upon the nature of the adsorbent and the amount of mixture to be separated. In ordinary chromatography a tube should be chosen with such a diameter that the amount of adsorbent used will form a column considerably longer than it is wide; ordinarily the ratio length: width from 3:1 to 10:1 is satisfactory. Efficient countercurrent contact of adsorbent with solution demands that the column have length; the requirement that the zones be sufficiently spread apart also requires length, as does ease in packing the adsorbent. The longer the column the slower the flow of liquid through it under a given head of pressure; hence with a given weight of adsorbent one has to balance the height (and width) of the column in order to obtain the best flow of liquid consistent with an adequate separation of zones. Also, long columns may be difficult to extrude. Data bearing on this problem are given below. Very short columns may be used for special purposes, as in frontal analysis, but here complete separation of zones is not obtained. Very wide columns may be difficult to pack, and often tend to give irregular fronts. However, this difficulty can be circumvented.[53]

The choice of *the adsorbent to be used* in a given separation may be approached on the basis of the data and generalizations of Chapters III and IV, where the relations between extent of adsorption and solubility, structure, and functional groups of substances are discussed. Chapter VII and the tables of adsorbents may be helpful, but usually the choice will have to be made finally through analogy and by trial.

What is needed is an adsorbent that will adsorb the components of the mixture to be separated. But it must not adsorb them too firmly, otherwise the development of the chromatogram will be impeded. The most satisfactory sort of adsorbent is one which differentiates between the components of the mixture, and an adsorbent which is very active may not do this effectively, since the strong general adsorption may overshadow small differences between individual adsorptions. It is evident that the approach to the choice of an adsorbent must at present be largely empirical when new mixtures are being examined. The choice of adsorbent is often made concomitantly with the choice of solvent.

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[52] Mair and Forziati, *J. Research Natl. Bur. Standards*, 32, 151, 165 (1944); Mair, *ibid.*, 34, 435 (1945); Mair, Gaboriault, and Rossini, *Ind. Eng. Chem.*, 39, 1072 (1947); Mair, *Ann. N. Y. Acad. Sci.*, 49, 218 (1948); Berg, *Trans. Am. Inst. Chem. Eng.*, 42, 665 (1946); R. Williams, Jr., and Hightower, *Chem. Eng.*, 1948, November.

[53] Claesson, *Arkiv Kemi, Mineral. Geol.*, A23, No. 1 (1946); Hagdahl, *Acta Chem. Scand.*, 2, 574 (1948); Mair, *J. Research Natl. Bur. Standards*, 34, 435 (1945).

The question of *how much adsorbent is needed* for a given separation can be answered upon recourse to several kinds of data. If the isotherms of the substances to be separated are known, or can be estimated by analogy from those of other substances then the following method may be used. From the concentration and amount of each substance there is estimated the weight of adsorbent which would just hold it as a zone with uniform maximum concentration. These weights are all added together to give the weight of adsorbent which would form a column over which the mixture would be spread, each component forming a zone with sharp boundaries and no spaces between the zones. This gives approximately the minimum amount of adsorbent needed. But zones tend to tail off so that extra adsorbent must be allowed for this. On the other hand, strongly adsorbed substances tend to displace weakly adsorbed ones and this would lessen the tailing of the weakly adsorbed ones. If, then, the mixture is a simple one, and the components widely different in adsorption affinity, then the minimum amount of adsorbent as calculated above is safe to use, or this + 10%. However if the mixture is complex or the components very similar, more adsorbent and a longer column will be needed.

The decision about *how long a column is needed* for a given weight or volume of adsorbent is a comparatively simple one to make. This decision is governed by several considerations. For a given weight of adsorbent and degree of packing, the longer the column and hence the narrower, the slower will be the flow of liquid, but on the other hand the greater will be the ease of separating the zones. LeRosen[54] found that the velocity of flow of developer solvent through columns of calcium hydroxide varied directly with the pressure difference between the ends of the column and inversely with the length of the column, but was largely independent of the diameter of the column. Diameters of 17, 43, and 70 mm. gave almost equal velocities of flow (mm./min.) for the same length of column. As the liquid was passed into the dry column the velocity of flow decreased until it became constant soon after the liquid passed the bottom of the column. The velocity of flow when a state of constant velocity has been reached is designated V_c. This velocity is influenced by the nature and particle size of the adsorbent, the nature of the solvent and of the substance adsorbed, and also by the degree of packing of the adsorbent (see below).

Cassidy[55] found that columns prepared from one gram of charcoal

[54] LeRosen, *J. Am. Chem. Soc.*, 64, 1905 (1942).

[55] Cassidy, *Dissertation*, Yale University, 1939.

each and packed in tubes 13, 16, and 23 mm. in diameter gave liquid chromatograms with exactly the same concentration profiles when treated with 0.3 g. of lauric acid dissolved in 100 ml. petroleum ether and developed with petroleum ether. The rates of flow (cc/min.) were in the order 23 mm. $>>$ 16 mm. $>$ 13 mm. Weil-Malherbe[56] says that with a given quantity of adsorbent the ratio of length of column to diameter may be varied between about 5 and 20 without much effect on the concentration profile of the zone. Mair[57] found that the sharpness of separation between aromatics and nonaromatics on certain silica gels did not depend significantly on the rates of flow, which were varied from x to 19 x. These factors were also investigated by LeRosen.[58]

It is apparent that the shape of the column is not a very critical factor in the separation. As mentioned before, extremely long columns flow too slowly to be satisfactory, while with very wide shallow ones the opportunity for separation of zones is decreased and the irregularities of flow between center and edge of the column may be great, tending to make the faces of the zone "fuzzy" (see above). The effect of too short a column is similar to that of an adsorbent with too large particle size.

The formation of the initial zone (in the application of the mixture to the column) will be affected to some extent by the *solvent* chosen to carry the mixture on to the column. An empirical approach is often necessary here. Several alternatives usually present themselves: the solvent to be used in carrying the mixture on to the column can be that in which the mixture was worked up (*e.g.*, as an ether solution after an extraction process) which, after serving its purpose of applying the substance to the column, will be followed by the chosen developer; the mixture can be transferred directly into the developer (if not already in it) before application to the column; the mixture without any solvent or developer present may be applied to the column; or the mixture may be deposited on a disk of filter paper, or in some other carrier which is laid on the top of the column of adsorbent and then covered with a thin layer of adsorbent.

The considerations applying to any solvent which may be used apply also to the developer. The question of the choice of developer will be taken up next.

There is one fairly good rule which can be applied to the *choice of a general developer*. This is to choose a solvent in which the components of the mixture are not too soluble. This is usually a solvent with a low molecular weight. To go with this one chooses an adsorbent which adsorbs the solvent somewhat, but not too strongly. If the solvent is adsorbed to some extent it helps to ensure that the components of the mixture to be adsorbed will not be too firmly bound. Fine differences in chromatographic effectiveness may be achieved by the use of a given adsorbent with given developer solvents which are members of an homologous series, or which are corresponding compounds, or solutions of graded concentration[59] (see Chapter V).

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[56] Weil-Malherbe, *J. Chem. Soc.*, 1943, 303.

[57] Mair, *J. Research Natl. Bur. Standards*, 34, 435 (1945).

[58] LeRosen, *J. Am. Chem. Soc.*, 69, 87 (1947); *Ind. Eng. Chem., Anal. Ed.*, 19, 189 (1947).

If a developer turns out in use to be not satisfactory one can either change to another developer or else modify the one in hand. Modification usually involves addition to the liquid of some substance which acts to expedite (or to delay) development. A frequent need is for more rapid development of the column, which can be obtained by adding to the developer a more strongly adsorbed substance, either preparing all of the developer of the same concentration or else adding the more strongly adsorbed substance in *gradually increasing amounts* so that the displacing effect of the developer steadily rises. The intention here is to force the segregation of zones in the column by gradually increasing the eluting power of the developer. One may thereby cause the zones to march consecutively out of the column. This method is in fairly common use. Sometimes the order of already partially separated zones may be changed by a developer, which may cause some confusion even though eventual good separation with a different order of zones may be obtained.[60] Strain has found many striking examples of this effect.[61] An example of the use of developer of graded strength is given in Chapter V.

A quantitative approach to the measurement of developing power has been made by LeRosen.[62] He defined a quantity R as the velocity of movement of the zone of adsorbed substance in millimeters per minute divided by the rate of flow of developer solvent. When such a quantity is known for a number of substances singly and in mixtures, and for a number of solvents and adsorbents, it becomes possible to choose a developer with some precision, for then one can be chosen which gives with the proper adsorbent the best spread of R values. With this information it is possible to decide, also, *how much developer* to use. Information of this kind allowed LeRosen to predict inversions of relative positions of zones of certain pairs of carotenoids with different adsorbents.

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[59] See papers by Reichstein and co-workers, *Helv. Chim. Acta,* 19, 1382 (1936); 22, 1212, 1222 (1939); 24, 247E (1941); 31, 688, 883, 1630, 1655 (1948); and Ruzicka and co-workers, *ibid.,* 31, 818, 1159, 1319 (1948); and earlier and later papers by these and other authors from these laboratories.

[60] Duschinsky and Lederer, *Bull. soc. chim. biol.,* 17, 1534 (1935); Strain, *J. Phys. Chem.,* 46, 1151 (1942); LeRosen, *J. Am. Chem. Soc.,* 64, 1905 (1942); Strain Manning, and Hardin, *Biol. Bull.,* 86, 169 (1944); Schroeder, *Ann. N. Y. Acad. Sci.,* 49, 204 (1948).

[61] Strain, *Ind. Eng. Chem., Anal. Ed.,* 18, 605 (1946).

[62] LeRosen, *J. Am. Chem. Soc.,* 64, 1905 (1942).

The development process may be very sensitive to foreign materials in solvents. Solvents prepared from new sources or "purified" by azeotropic distillation may contain traces of impurities which, though present in amounts ordinarily considered inappreciable, are able to make themselves felt if the liquids are used in chromatography.[63]

Tiselius[64] has given a simple theoretical background to the choosing of developers. His method of *displacement analysis,* which exemplifies this theory, is described below. Displacement analysis is a special case of development in which a developer mixture is used to displace less well adsorbed substances from the adsorbent so that these may be made to migrate out of the column in an orderly fashion, in a consecutive series of zones, and without appreciable tailing-off (Fig. VIII-14). To obtain this result one has to choose the developer rather carefully. In the ideal case the displacing substance sets up, as demonstrated by Tiselius, a state stationary with respect to the concentration of the zone. The zones then move down the column and out into the solution with well-defined boundaries. The displacer substance which is added to a solvent to produce the developer must be more strongly adsorbed than any of the substances in the zones which are to be developed. When it is applied to the column it dislodges even the most strongly adsorbed molecules, which move onward and displace, perhaps with aid from the developer, the next more strongly adsorbed ones, and so on along the column. The displacer acts as a sort of "piston." A higher homolog of the substances being separated, or some substance of totally different chemical nature, may serve as a developer.[65] The operation of the developer can be visualized by means of a diagram given by Tiselius (Fig. VIII-15). This diagram shows the isotherms of four substances to be separated, A, B, C, and G, and of the displacing substance, D. It is apparent that the four substances are less well adsorbed than the displacer. If the displacer is used at a concentration c_D, then it will have a certain adsorption coefficient a_D which will govern the rate of migration of its zone along the column, as will be evident from the discussion above under "frontal analysis." If a stationary state is to be set up so that the zones of A, B, and C move out of the

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[63] Thomas, *Ann. N. Y. Acad. Sci.,* 49, 161, 179 (1948); Anonymous, *Nature,* 157, 487 (1946).

[64] Tiselius, *Arkiv Kemi, Mineral. Geol.,* A16, No. 18 (1943).

[65] Claesson, *Arkiv Kemi, Mineral. Geol.,* A23, No. 1 (1946); Hagdahl and Holman, *J. Am. Chem. Soc.,* 72, 701 (1950).

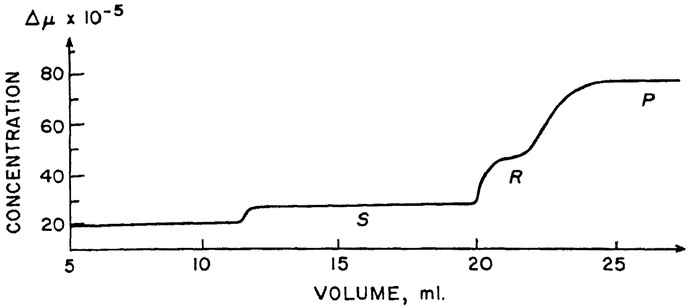

Fig. VIII-14. Displacement analysis.[64] The concentration (in terms of refractive index) is plotted against the volume passing the foot of the column.

The developer, *P*, is 0.25% phenol, which displaces raffinose, *R*, which displaces sucrose, *S*. These two substances are segregated into separate zones. Under standard conditions the height of the zone characterizes the substance; the length of the zone measures the amount present.

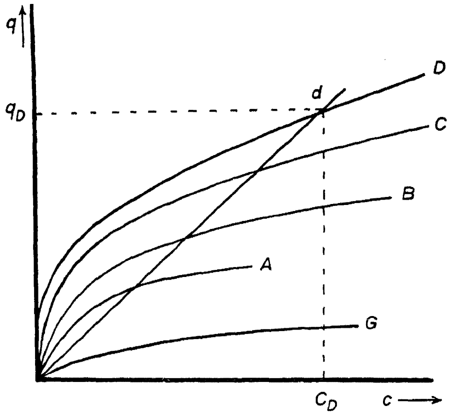

Fig. VIII-15. Theory of displacement analysis.[64] Isotherms of substances *A*, *B*, *C*, *D*, and *G* are shown.

The developer, *D*, of initial concentration c_D will have a certain adsorption coefficient α_D (the ratio q_D/c_D). This coefficient is represented by the line from *d* to the origin. Wherever it cuts an isotherm that substance at that concentration will show the same α. On this line, then, $\alpha_A = \alpha_B = \alpha_C = \alpha$, and once this stationary state is set up all the zones will move from the column in order, *A* ahead of *B*, etc. The component *G* is so poorly adsorbed that the line of constant α does not cut its isotherm. It moves on ahead of the other zones in the displacement analysis; see Figure VIII-18.

column ahead of D, and in order, without tailing off (Fig. VIII-14), then all of the zones must exhibit the same adsorption coefficient, their relative positions on the column being a function of their respective strengths of adsorption. The adsorption coefficient $a = (q/m)/c$, and this ratio

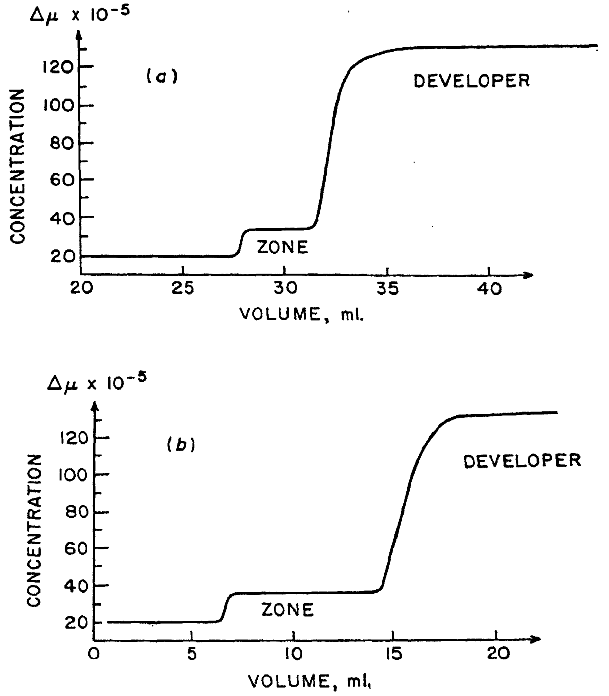

Fig. VIII-16. Displacement analysis showing the effect of increase in the concentration of a substance.[64]

(*a*) The substance which gives the step is 5 mg. sucrose. It is displaced with 0.5% aqueous phenol and is recovered to the extent of 95–98%. The same diagram is obtained with this amount of sucrose whether it is applied at initial concentration 0.05%, 0.1%, 0.5%, or 2.0%, provided that the displacer is kept at 0.5%. With 10 mg. of sucrose the step, as in (*b*), is twice as long.

is represented by the straight line from d to the origin in Figure VIII-15. The different zones will have the same coefficient at the points where this line cuts their isotherms. During the displacement development the concentrations of A, B, and C become adjusted to the stationary values imposed by the concentration of D and the zones segregate themselves. This latter action comes about in the way described in the early part of this chapter; the less well adsorbed molecules migrate faster than the more strongly adsorbed ones; also they are displaced by the latter. At a given concentration of developer the stationary state is fixed as regards the concentration of the various zones, so that the amount of each substance present governs the length of its zone. Thus, if twice as much of, say, *C* were present in a mixture otherwise the same, then the concentration of the zone would remain the same, but its length would be twice as great (Fig. VIII-16). Also considerable changes in the concentration in which *C* is applied to the column may be made without changing the concentration of the zone provided the concentration of the displacing substance

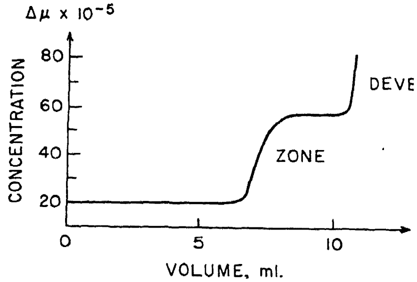

Fig. VIII-17. Displacement analysis showing the effect of increase in the concentration of the developer.[64]

10 mg. of sucrose is developed with 1.0% phenol. The height of the step is increased. Compare Figure VIII-16*b*.

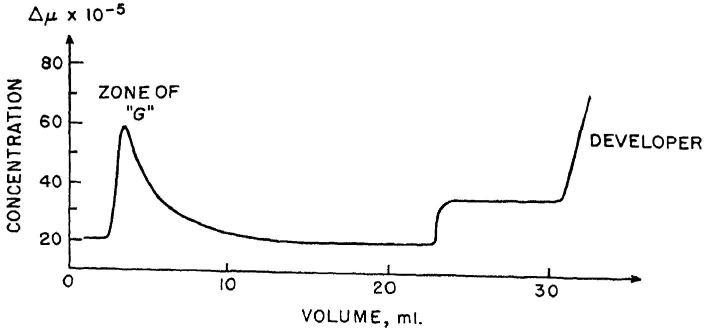

Fig. VIII-18. Displacement analysis showing the behavior of a substance ("*G*") which runs so fast that it is not influenced by the developer.[64] The isotherm of this substance on this adsorbent is not cut by the line of constant *a*. A similar substance is shown at *G* in Figure VIII-15.

is kept the same. But if the concentration of the displacer is increased then the concentration of the zone is increased, as would be expected from the theory (see Fig. VIII-17). It follows also that once the stationary state has been set up the concentration profile of the zone is independent of the length of the column or of the amount of developer used. However, a certain minimum length of column is necessary so that the setting up of the stationary state and the segregation of the zones can occur. With more strongly adsorbed substances a shorter column can be used (less adsorbent) than with less strongly adsorbed ones. Very weakly adsorbed substances, the isotherms of which do not cut the "line of constant a" such as G in Figure VIII-15, may migrate out of the column ahead of the serried zones (Fig. VIII-18). In such zones the typical sharp front and tailing-off of the rear boundary is observed. This subject has been clearly presented by Claesson.[66]

The *choice of an eluent* usually presents no difficulty (see Chapter V). It is governed by a few simple and obvious rules, and these are easily applied. As eluent a liquid is chosen which is a good solvent for the component to be eluted. The eluent may be itself well adsorbed, so that its solvent action is abetted by its displacing action at the interface; or one may add to the eluent some strongly adsorbed substance to promote this displacement. One further requirement of the eluent is that it be easily removable from the desorbed component; basic or acidic solvents may be used to elute stable neutral substances, or neutral solvents, to elute basic or acidic substances; low-boiling eluents may be used to elute high-boiling substances. The problem is a famliar one.

Implicit in the above discussion is the understanding that adsorbent, solvent, developer, and eluent should not react adversely with the substance to be separated. (See below under the discussion of the limitations of the chromatographic method.)

V. MANIPULATIONS AND PHENOMENA

The various manipulations in the process of chromatography will now be discussed, and it will be necessary to make further remarks about the adsorbent, developer, and eluent.

The adsorbent has to be packed in the Tswett tube in the form of a *column* (other arrangements were mentioned above). Here two objectives must be met: the adsorbent must be evenly packed so that the zones will maintain a regular contour as they are developed, and the adsorbent must allow the passage of the liquid. The first of these objectives may be reached by several paths, each of which has its advantages. The adsorbent may be mixed with developer or other liquid to form a slurry which is then poured into the tube and allowed to drain (with or without suction or pressure). This method of forming the column is widely applicable and usually very satisfactory. If the adsorbent is inhomogeneous with respect to particle size then the slurry should be fairly thick in order to avoid stratification in the resulting column, or the slurry may be added to the tube in small portions, each being sucked nearly dry before the next is added. (However, suction may produce air spaces at the bottom of the column.) Levy[67] places the slurry in a separatory funnel with a stirrer, and allows it to flow into the clean, dry tube. Another procedure is to place the solvent in the tube which has been stoppered at the bottom and then to sift into it the dry adsorbent. One thus forms a column by a process of even sedimentation, and the solvent may be later sucked off to the extent desired. Finally, one may form the column by packing the dry adsorbent into the tube. This must be done rather carefully. The adsorbent is introduced in small portions and is packed evenly with a dowel which is somewhat smaller than the chromatography tube, attention being paid to the portions of adsorbent near the walls of the tube (Zechmeister[68] suggests that the packing is facilitated and the results improved if the dowel is slightly concave at the face used for packing). The packing of the portions of adsorbent is done with gentle pressure and with, or without, accompanying suction. It is convenient to hold the dowel in one hand, and the tube in the other; to press gently, release, rotate tube a little, and press again. Proficiency in packing columns usually requires some practice.

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[66] Claesson, *Arkiv Kemi, Mineral. Geol.*, **A23**, No. 1 (1946); *Ann. N. Y. Acad. Sci.*, **49**, 183 (1948).

The uniformity of packing in a column may be estimated by measuring the length of column needed to contain a unit volume of liquid and dividing this by the length of tube required to contain the same volume.[69] This yields a quantity S which gives a measure of the fraction of the tube volume occupied by the adsorbent, $(S - 1)/S$. LeRosen[69] found S to vary from an average of 1.97 for the top third to 1.79 for the bottom third of certain calcium hydroxide columns. In silicic acid–Celite mixtures, S bore a linear relation to the weight fraction of silicic acid (or Celite).[70]

The second objective in preparing a good column is to obtain one through which liquid will flow with reasonable speed. This requires that the column not be packed too tightly. However, where very finely divided adsorbents are being used it is often extremely difficult to avoid such close packing that the passage of liquid is undesirably impeded. Also, during the course of the chromatography it sometimes happens that the suction or pressure applied to aid flow, and which are initially of some use, eventually lead to a compacting of the column. There are three solutions to such difficulties. One solution is to use an adsorbent in the form of coarse particles, or, better, to use a mixture of mesh sizes. This is often very helpful, but it cannot be carried to an extreme, for if the particles become too coarse their relative surface area will be greatly diminished and their adsorbing capacity per gram of adsorbent will consequently be lessened. Also, sharpness of fronts may be impaired.

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[67] Levy, *Chemistry & Industry*, 1945, 380; *Chem. Abstracts*, 40, 1080 (1946).

[68] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography*. Wiley, New York, 1943.

[69] LeRosen, *J. Am. Chem. Soc.*, 64, 1905 (1942).

[70] LeRosen, *J. Am. Chem. Soc.*, 67, 1683 (1945).

Fairly wide differences are found in the particle sizes of the adsorbents used in chromatography. Zechmeister and Cholnoky[71] list a number of adsorbents and their "average particle sizes." These vary from about 1.5 to 10.5 microns. Since 1 micron equals 0.001 mm., powders such as these would be finer than that which just passes a 325-mesh sieve, the openings of which are 0.043–0.044 mm.[72] Of one sample of a commercial alumina standardized for chromatographic adsorption analysis somewhat more than 30% passed a 300-mesh sieve. LeRosen[69] found a satisfactory range of V_c (velocity of flow of developer solvent in millimeters per minute through the column when a state of constant flow has been reached, see above) with calcium hydroxide columns to be associated with an average particle size of 5 to 15 microns. The range of V_c was 5 to 15 mm./min.

It is not easy to increase the particle size of an adsorbent which is found to be too finely divided. Sometimes the adsorbent can be "granulated" by moistening to a dough, pressing through a sieve, and drying. Other expedients may have to be employed. One possible expedient is to use a shorter column (for a given weight of adsorbent, to use a wider tube) or to use a greater pressure difference between the ends of the column. Excessive pressure differences (greater than, say, 1 atm.) are usually of little avail, as mentioned above; however, the use of a shorter column does improve the situation. Limitations in the length of the column have already been discussed.

A third method of improving the rate of flow of liquid through the column is by the use of a filter aid. This was first suggested by Strain,[73] and has proved to be most useful. The common filter aids are inert materials which give bulk and porosity to a column. The filter aid serves at least two purposes: it facilitates the operation of packing the dry column and it improves the rate of flow of developer through the finished column. The operation of packing is facilitated by the filter aid because it acts as a "bulking agent." The adsorbent is diluted so that a given weight of it can be distributed over a longer and wider column. A more uniformly packed column is the result. Also, when adsorbent is mixed with the filter aid it seems that the resulting mass packs more smoothly. The dry adsorbent may be mixed with the filter aid by agitating the two in an Erlenmeyer flask. Common filter aids are diatomaceous earths. They are available in a number of grades (Chapter VII).[74]

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[71] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography*. Wiley, New York, 1943.

[72] *Handbook of Chemistry*, N. A. Lange, ed., Handbook Publishers, Sandusky, 7th ed., 1949, pp. 882–884.

[73] Strain, *J. Biol. Chem.*, **105**, 523 (1934).

A word of caution is necessary here. The filter aid to be used as an adjunct to a chromatographic separation should be tested for soluble material.[75] (Cassidy[76] found that 15 g. of a sample of filter aid, refluxed with 300 ml. of petroleum ether for 2 hrs. yielded 1.7 mg. of nonvolatile extractive. Analytical grades of filter aid now available should give no trouble.) Also, it should be tested for adsorbing power because, although these substances may be found to be inert in some cases (they do not adsorb higher fatty acids from petroleum ether[77]), it is known that in other instances they may act as adsorbents[78], they have been used to adsorb sex hormones from urine[79] and some tend to adsorb streptomycin.[80] If filter aids are not available, or are for some reason undesirable, one may use instead some inert or weakly adsorbent substance such as calcium carbonate (but calcium carbonate adsorbs some substances) which can be obtained in a coarse condition and which, mixed with the adsorbent, can increase the porosity of the column. Fine sifted sand, or ground glass may be useful. Wachtel and Cassidy[81] used filter paper pulp as an inert "bulking agent" for forming columns of charcoal for separating amino acids in water solution. A mechanical egg beater was used to mix the filter paper pulp and charcoal with water to form a slurry.

That the filter aid improves the rate of flow in columns over the rate with the pure adsorbent is general experience. LeRosen[82] has provided quantitative data on the effect of admixture of a filter aid (Celite 535) with an adsorbent (silicic acid, Merck). In these particular experiments S, which is a measure of the degree of packing (see above) was found to be a linear function of the weight composition of the mixture, and decreased with increase in the fraction of filter aid; $\log_{10}$ of the rate of flow of developer (V_c) bore a straight-line relation to the volume fraction of filter aid, it increased with increase in fraction of filter aid; R, the rate of movement of a zone (of *p*-nitraniline) relative to the rate of flow of developer (benzene) increased very rapidly with increase in ratio of filter aid present. These relations would be expected to hold for other adsorbents, developers, and adsorbed substances.

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[74] Wilkes, *Ind. Eng. Chem., Anal. Ed.*, 18, 329 (1946).

[75] Strain, *Nature*, 137, 946 (1936).

[76] Cassidy, *Dissertation*, Yale University, 1939.

[77] Cassidy, *J. Am. Chem. Soc.*, 62, 3076 (1940).

[78] Strain, Manning, and Hardin, *Biol. Bull.*, 86, 169 (1944); Riley, *Science*, 107, 573 (1948); Riley, Hesselbach, Fiala, Woods, and Burk, *ibid.*, 109, 361 (1949).

[79] Gallagher, Koch, and Dorfman, *Proc. Soc. Exptl. Biol. Med.*, 33, 440 (1935).

[80] Silcox, *Chem. Eng. News*, 24, 2762 (1946).

[81] Wachtel and Cassidy, *Science*, 95, 233 (1942); *J. Am. Chem. Soc.*, 65, 665 (1943).

[82] LeRosen, *J. Am. Chem. Soc.*, 67, 1683 (1945).

The column of adsorbent is conveniently *formed on* a pad of cotton or of glass cotton[83] supported near the bottom of the Tswett tube by a perforated or fritted plate which is sealed in or which rests upon a constriction or upon indentations. Whatever is used, the object is to prevent the escape of adsorbent from the tube. It is advisable to ascertain that the pad of cotton or other material does not act as an independent adsorbent.

The substance to be separated may be *applied to the adsorbent* with or without dilution if it is a liquid; if it is a solid it must eventually be brought into solution. Kaufmann[84] has applied liquid fatty acids directly to columns of various adsorbents and obtained separations. The more common practice, however, is to use a solvent to carry the substances which are to be chromatographed on to the column. The question then arises: is it better to apply the mixture to be separated to the column in concentrated or in dilute solution. Adsorption is *relatively* greater from more dilute than from more concentrated solutions. Since the countercurrent method takes utmost advantage of the capacity of the adsorbent, a solution of a substance which can only be obtained in a dilute form can sometimes be advantageously concentrated by passing it through a column of adsorbent which is chosen especially for its retentive ability.[85] In such a case as this no alternative was initially present. The concentrated material can then be eluted into a small volume. When alternatives do exist, when a concentrated solution is available so that it may be applied directly to the column or diluted first, then it is usually advisable to use the concentrated, although some substances may crystallize out when developer is added. This gives the opportunity of getting a compact initial zone with the least amount of adsorbent. The developer has some subsequent influence on the concentration of the zone increasing, or decreasing it

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[83] Englis and Fiess, *Ind. Eng. Chem.*, 36, 604 (1944).

[84] Kaufmann, *Fette und Seifen*, 46, 268 (1939).

[85] Koschara, *Ber.*, 67, 761 (1934); *Z. physiol. Chem.*, 229, 103 (1934).

(see under *displacement analysis,* above). The use of a concentrated solution in which to apply the mixture to the column does not imply that the solvent in which a concentrated solution can be made will make a good developer. A more subtle difficulty may arise with concentrated solutions if multilayer adsorption should be produced. Here the specificity of the process would be lost in second or higher layers and hence poorer separations might occur. This is a difficulty occasionally found with other methods, such as crystallization of fatty acids from nonpolar solvents, where heterogeneous dimerization hinders separation, or in the lead salt–ether methods for separating saturated from unsaturated acids.

The important object of chromatography is the *formation of zones.* There are a number of aspects of the processes which lead to zone formation which need now to be discussed. These are the recognition of the zones (the shapes concentrationwise, of the zones), their rates of movement, and the factors which influence them. This will require also some further discussion of adsorbents and developer solutions.

The *recognition of zones* is, of course, easy if the substances adsorbed are colored or become colored upon adsorption. It becomes difficult with colorless substances. Here various expedients have been contrived for recognizing and delineating the zones. The zones may be sought either in the column or outside of the column. In the former case they are found as more or less well-defined regions wherein various components of the original mixture are adsorbed separately. In the latter case they are observed as volumes of percolate which differ from previous and following volumes.

If *colored substances* are being separated upon the column, then it is common practice to use a white or light-colored adsorbent. In the developed chromatogram the zones are then seen as distinct regions, each with its own color. But one may also use dark-colored adsorbents such as charcoal. In this case the zones must be washed through the column. They are recognized as portions of colored solution which flow from the column, each with its own color, and in favorable cases quite separated from other zones by portions of colorless liquid. However the zones may not be discrete, but may overlap to some extent. Again the overlapping portions can be observed visually.

It is evident that color in the substance to be separated brings considerable simplification to the chromatography for if the zones can be seen one knows at once what is going on in the column. However, most substances are not colored, and if chromatography were restricted to colored substances it would be of limited use indeed. Fortunately, there are many ways in which the method can be amplified so that it may be used with colorless substances. These methods will be dealt with below, treating, for ease of discussion, first, those methods which detect zones on the adsorbent and then those methods which apply to the liquid as it emerges from the column.

One method of dealing with colorless compounds is to convert them, before chromatographic separation, into *colored derivatives*. This method was originated by Strain[86] who separated carbonyl compounds in the form of colored derivatives (2,4-dinitrophenylhydrazones, etc.) on a number of adsorbents. It has since found further use in the same application[87] and in the separation of sterols[88] and of sugars[89,90] in the form of their respective azoyl esters. One difficulty with this general method is that the groups which may be used to bring color to the derivative may be so large, or may have such a strong adsorption, that they may overshadow the differences between the colorless molecules to be separated.[91] However, the method is an important one and appears to be useful in some fields. For example, Coleman and his co-workers[90] prepared colored *p*-phenylazobenzoyl esters of simple sugars, or of the products of hydrolysis and alcoholysis of methylated disaccharides, and separated them chromatographically.

The *brush method* is one applicable to many types of colorless compounds. It was devised by Zechmeister and his co-workers.[92] The requirement for this method is that the substances to be separated give a color test of some kind (a colored product or a fluorescent derivative) with some reagent. The developed column, developed empirically, is extruded from the tube and streaked lengthwise with a brush dipped in the test reagent. The colors appearing on the surface of the column at the place touched by the reagent indicate the positions of the zones. These can then be separated from each other and from the rest of the adsorbent. That part of the adsorbent containing the color test can readily be shaved off, so that it may be discarded. Crowell and König have devised a slotted tube which may be opened and reclosed during the course of an analysis in order to gain access to the adsorbent. With this device, brush or spot tests could be made to follow the course of the development process.[93] The brush method has been used to recognize zones formed by *cis* and *trans* isomers[94] and zones formed by carbohydrates and their derivatives.[95] In both cases alkaline permanganate was used as the streak reagent. Other reagents and their uses in the chromatography of sugars and related substances are given by Binkley and Wolfrom.[96]

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[86] Strain, *J. Am. Chem. Soc.*, 57, 758 (1935).

[87] Lucas, Prater, and Morris, *J. Am. Chem. Soc.*, 57, 723 (1935); Buchman, Schlatter, and Reims, *ibid.*, 64, 2701 (1942); Roberts and Green, *Ind. Eng. Chem., Anal. Ed.*, 18, 335 (1946); Johnston, *Science*, 106, 91 (1947).

[88] Ladenburg, Fernholz, and Wallis, *J. Org. Chem.*, 3, 294 (1938).

[89] Reich, *Compt. rend.*, 208, 589, 748 (1939); *Biochem. J.*, 33, 1000 (1939).

[90] Coleman and Farhnam, *Proc. Iowa. Acad. Sci.*, 48, 246 (1941); Coleman, Farnham, and Miller, *J. Am. Chem. Soc.*, 64, 1501 (1942); Coleman, Rees, Sundberg, and McCloskey, *ibid.*, 67, 381 (1945).

[91] Cassidy, *J. Am. Chem. Soc.*, 63, 2735 (1941), footnote 5.

[92] Zechmeister, Cholnoky, and Ujhelyi, *Bull. soc. chim. biol.*, 18, 1885 (1936); Zechmeister and Frehden, *ibid.*, 22, 458 1940.

The position of the zone may be marked by means of a *marking substance* which is adsorbed on the column in a position in known relation to that of the colorless but desired substance. Brockmann[97] used this method for the isolation of vitamin D from tuna fish liver oil. A dyestuff, "indicator red 33" (later reported to be Sudan III), was found which when mixed with the concentrate from the liver oil and adsorbed on an alumina column (from benzene–petroleum ether 1:4 and developed with this mixture) apeared at the same place as the vitamin D. This mixed zone could be separated out, and after desorption the indicator could be removed by extraction with alkaline methyl alcohol.

In another method an *indicator* is incorporated with or on the adsorbent. The adsorption of the substance causes a local and reversible change in the color of the indicator, which thus marks the zone. This is the method introduced very successfully by Martin and Synge[98] in the separation of acetylated amino acids by "partition chromatography" (Chapter X). It was used by Graff and Skau,[99] who were able to separate stearic and oleic acids on a column of magnesium oxide which had been colored with the indicator phenol red. Petroleum ether was used as the developer. The indicator changed from pink to yellow in the regions of the zones, thus showing their boundaries. Sylvester, Ainsworth, and Hughes[100] tinted alumina with bromothymol blue and used such columns to separate traces of fatty acid from unsaponifiable matter, using chloroform or ether as developer.

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[93] Crowell and König, *Ind. Eng. Chem., Anal. Ed.,* 16, 347 (1944).

[94] Zechmeister and McNeely, *J. Am. Chem. Soc.,* 64, 1919 (1942).

[95] McNeely, Binkley, and Wolfrom, *J. Am. Chem. Soc.,* 67, 527 (1945); Lew, Wolfrom and Goepp, *ibid.,* 67, 1865 (1945); 68, 1449 (1946); Binkley and Wolfrom, *ibid.,* 68, 1720 (1946); Georges, Bower, and Wolfrom, *ibid.,* 68, 2169 (1946); and later papers.

[96] W. W. Binkley and M. L. Wolfrom, "Chromatography of Sugars and Related Substances," *Scientific Report Series No. 10,* Sugar Research Foundation, Inc., New York, 1948. See also p. 264, footnote 197.

[97] Brockmann, *Z. physiol. Chem.,* 241, 104 (1936); 245, 96 (1937); Brockmann and Busse, *ibid.,* 249, 176 (1937).

[98] Martin and Synge, *Biochem. J.,* 35, 1358 (1941).

[99] Graff and Skau, *Ind. Eng. Chem., Anal. Ed.,* 15, 340 (1943).

[100] Sylvester, Ainsworth, and Hughes, *Analyst,* 70, 295 (1945).

Somewhat related to this is the *fluorescent adsorbent* method. The fluorescent adsorbent may be prepared by adsorbing fluorescent substances onto the adsorbent (salicylic acid, etc., onto alumina; berberine onto silica gel; etc.[101]) or by diluting the adsorbent with a suitable finely powdered fluorescent material.[102] Sease[102] prepared a fluorescent silica by mixing into Merck reagent silicic acid 2.5% of No. 62 zinc sulfide.[103] (Various other mixtures and fluorescent additives are given in the original papers.) Zones of certain colorless nonfluorescing adsorptives then could be observed where they quenched the fluorescence of the adsorbent.

Sometimes a substance *changes* or *develops color* when adsorbed, and thus marks its own zones. Holmes, Corbet, and Cassidy[104] observed that carotene on certain gels produced a green color. Kobayashi and Yamamoto[105] had observed the formation of color when vitamin A containing substances were adsorbed on acid clays.

An exceedingly useful technique for detecting certain colorless zones was developed by Karrer and Schöpp[106] and by Winterstein and Schön.[107] It involves examining the chromatogram under filtered *ultraviolet light.* Fluorescent substances, colorless under ordinary light, may then show up and the course of the development may be easily followed. It is convenient to use the light from a quartz mercury arc lamp filtered with Wood's glass.[108] It is usually not necessary to use quartz tubes for the columns. The column may be examined either in the tube or else after extrusion. It should be mentioned that some adsorbents are themselves fluorescent, and that adsorption may change the color of fluorescence of a substance even as it may change the color under visible light (see above).

An interesting way in which colorless substances can sometimes become visible on a column has been observed by Trappe.[109] He noted that silica gel columns became translucent when wetted with certain solvents and under these conditions it was possible to observe zones formed by colorless substances. The substances changed the light transmission of the column in the region where they were adsorbed—one sees, so to speak, the simulacrum of a colorless zone on a colorless adsorbent. Another observation which probably belongs in this category was reported by Myers and co-workers.[110] They found that columns of the acid-binding resin Amberlite IR-4[111] showed distinguishable zones when treated with mixtures of hydrochloric and sulfuric acids, and that these acids could be separated to some extent upon such columns. An analogous observation with glutamic acid was made by Cleaver, *et al.*[112] Claesson[113] has suggested that otherwise invisible zone boundaries may be detected by total reflection of light entering through a thick glass wall of the adsorption tube.

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[101] Brockmann and Volpers, *Ber.*, 80, 77 (1947).

[102] Sease, *J. Am. Chem. Soc.*, 69, 2242 (1947); 70, 3630 (1948).

[103] Patterson Screen Division, E. I. du Pont de Nemours & Co., Inc., Towanda, Pa.

[104] Holmes, Corbet, and Cassidy, 1932, *unpublished data*; Cassidy, *Thesis*, Oberlin College, 1932; Holmes and Corbet, *J. Biol. Chem.*, 127, 449 (1939).

[105] Kobayashi and Yamamoto, *Mem. Faculty Sci. Eng., Tokyo,* 4, 23 (1927); *Chem. Abstracts,* 22, 2397 (1928).

[106] Karrer and Schöpp, *Helv. Chim. Acta,* 17, 693 (1934).

[107] Winterstein and Schön, *Z. physiol. Chem.*, 230, 139 (1934).

[108] Sease, *J. Am. Chem. Soc.*, 69, 2242 (1947); 70, 3630 (1948)—used for various purposes: an argon glow lamp (Cenco No. 71370, complete with ultraviolet filter); an incandescent ultraviolet lamp (Purple X, General Electric Co., no filter used); and the hydrogen lamp from a Beckman spectrophotometer (this was the most generally useful since it has the widest range).

[109] Trappe, *Biochem. Z.*, 306, 316 (1940).

Two of these methods may be combined. For example, Kirchner, Prater, and Haagen-Smit[114] prepared fluorescent derivatives of colorless, nonfluorescent substances (*p*-phenylphenacyl esters of lower fatty acids, which could be separated on silicic acid from 1:1 benzene–ligroin) which could then be observed during chromatographic separation.

All of these methods are useful in their places for indicating zones within the Tswett tube or in the extruded column. Some of them as will have been apparent, may also be used to find differences in the concentration or solute content of the liquid issuing from the column. If in a given case none of these is applicable and no others can be devised, then recourse must be had to an empirical procedure. The development is carried to a given point, usually at least to the point at which some substance appears in the percolate at the bottom of the column for this indicates that the entire column is being utilized, and then the column is extruded and cut up arbitrarily into an appropriate number of sections. The column may be cut into unequal sections "logarithmically," the larger ones at the bottom, if the substances being separated are homologs. (For this purpose the logarithmic rulings on the slide rule make a good guide.) The arbitrarily cut sections are then eluted and the eluate examined. Some of the fractions thus obtained may have to be recombined and rechromatographed.

Other methods may be conceived to follow the course of development of colorless substances. For example, a column with many sealed-in electrodes may be prepared so that the conductivity of the column may be scanned; or the column may be scanned for changes in dielectric effect using a device such as that reported by Troitskiĭ.[115]

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[110] Myers, Eastes, and Myers, *Ind. Eng. Chem.*, 33, 697 (1941); Myers, Eastes, and Urquhart, *ibid.*, 33, 1270 (1941).

[111] Resinous Products and Chemical Co., Philadelphia, Pa.

[112] Cleaver, Hardy, Jr., and Cassidy, *J. Am. Chem. Soc.*, 67, 1343 (1945).

[113] Claesson, *Nature*, 159, 708 (1947).

[114] Kirchner, Prater, and Haagen-Smit, *Ind. Eng. Chem., Anal. Ed.*, 18, 31 (1946).

[115] Troitskiĭ, *Biokhimiya*, 5, 375 (1940); *Chem. Abstracts*, 35, 4794 (1941).

One may employ another method of chromatography in which the zones are made to pass successively out of the tube, being then recognized by some change in the properties of the effluent liquid. This is a *liquid chromatogram.*[116]

The changes in properties of successive percolate volumes may be observed: by following changes in concentration of nonvolatile matter, by evaporating solvent from aliquots of the percolate and weighing the residues[117]; by changes in hydrogen ion concentration[116,118]; by change in refractive index[119] whether observed with a refractometer, interferometer, or by the use of the schlieren method[120]; by changes in conductivity[121]; or by almost any other physical analytical method. Tracer techniques have been utilized also, as described in Chapter IX.

Any applicable chemical method may be used, such as titration, color testing, or other means of spotting particular substances or distinguishing between various substances. Reagent paper strips can be used conveniently to test small drops of liquid at the foot of the column, or they may be attached to the tube as indicators of the appearance of a zone.[122]

Physiological test methods may also be used, as with vitamins, or plant or animal hormones, etc. Also taste or odor may be employed. The fundamental question is one of detecting and evaluating qualitative as well as quantitative changes in solutions. This introduces a consideration of concentration contours of zones, and the modifications which are produced during development.

When colored substances are chromatographed then the *shapes of the zones* can readily be observed and it is seen that the fronts of most zones are quite sharp, whereas the following boundaries often are not. With colorless substances one may plot concentration against volume of percolate in a liquid chromatogram and here too it is found that the leading boundary is relatively sharp while the following has a tendency to tail off. This situation may be portrayed graphically.[123] The curve so obtained is a projection of the chromatogram (Tiselius' phrase) out into the percolate fluid, and it serves to indicate the zones. A "zone" is recognized by an abrupt, rapid rise in concentration to a maximum value, followed by a tapering off (Fig VIII-8).

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[116] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography.* Wiley, New York, 1943.

[117] Cassidy, *J. Am. Chem. Soc.,* 63, 2735 (1941).

[118] Cleaver, Hardy, Jr., and Cassidy, *J. Am. Chem. Soc.,* 67, 1343 (1945).

[119] Tiselius, *Arkiv Kemi, Mineral. Geol.,* **B14**, No. 22 (1940); Tiselius and Claesson, *ibid.,* **B15**, No. 18 (1942); Claesson, *ibid.,* **A23**, No. 1 (1946); Dutton, *J. Phys. Chem.,* 48, 179 (1944).

[120] Tiselius, *Science,* 94, 145 (1941); Tiselius, in Kraemer, ed., *Advances in Colloid Science,* Vol. I, Interscience, New York, 1942, p. 81.

[121] Tiselius and Claesson, *Arkiv Kemi, Mineral. Geol.,* **B15**, No. 18 (1942); Thomas and Solomon, 1946 (unpublished).

[122] Zechmeister, *Ann. N. Y. Acad. Sci.,* 49, 145 (1948).

[123] Cassidy, *Dissertation,* Yale University, 1939; *J. Am. Chem. Soc.,* 63, 2735 (1941); Cassidy and Wood, *ibid.,* 63, 2628 (1941).

The *development* of the chromatogram involves the movement of the adsorbed substances in the direction of flow of developer liquid. Because of this movement the zones in a column may be observed to migrate down the column. It is of interest to discuss briefly the rate of this movement and the factors which influence it as well as the changes which may occur in the shape and position of the zone during its migration.

The postulated shapes of zones before and during development have been sketched by Caliri,[124] Strain,[125] and others (see theory, above) and one may certainly say, qualitatively, that during ordinary development the zones tend to become somewhat less sharp at their boundaries, and to become somewhat wider as they move down the column. The widening and tailing off has been discussed above under theory.

The intensity of a colored zone, or in general the maximum concentration reached on the adsorbent in a zone, is expected to be a function of the concentration at which the liquid is applied to the column. This is found to be so in a simple case[126] and is predicted by theory. It may also be a function of the distance along the column through which the zone has moved. It will also be influenced by any other substances present in the zone, since these will compete with the zone-forming molecules for the limited available surface of the adsorbent.[127] This means that the concentration of the adsorbed substance will depend on the solvent used, for the solvent is more than a vehicle for the solute—it competes with the solute for the interface. It also means that special solvents or mixtures which may be used to improve development may change the contour of the zone. The concentration contour of the zone, then, is not necessarily fixed during development, but is subject in many ways to change. This was discussed and examples of it given during the treatment of displacement analysis. A further reason why the choice of displacing agent is crucial may be derived from the observation that the order of zones in a column may be changed by a change in developer.[128] Such a change would obviously introduce complications into the procedure.

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[124] Caliri, "Recherches sur les relations entre l'adsorption mixte et l'analyse chromatographique," *Thesis*, Fribourg, 1940.

[125] Strain, *J. Phys. Chem.*, 46, 1151 (1942).

[126] Cassidy and Wood, *J. Am. Chem. Soc.*, 63, 2628 (1941).

[127] Tiselius, *Arkiv Kemi, Mineral. Geol.*, A16, No. 18 (1943).

[128] Strain, *Chromatographic Adsorption Analysis*, Interscience, New York, 1945; *Ind. Eng. Chem., Anal. Ed.*, 18, 605 (1946); Schroeder, *Ann. N. Y. Acad. Sci.*, 49, 204 (1948).

The discussion of the chromatography of mixtures has been largely directed to the means of obtaining separations which are as complete as possible. Such might be pursued for preparative or for analytical purposes, the goal being reached when 100% of each of the constituents of the mixture is obtained separate and in hand. However, chromatography may be used for analytical purposes without isolating the substances or even getting them all separated. This use was devised by Tiselius, and named "frontal analysis." The method has been described above. Chromatography may be used in another way. Complex mixtures of unknown composition may give characteristic patterns of zones in the chromatogram tube. Such a pattern might be used to characterize an industrial product, such as a fluidextract.[129] As an example, Valentin[130] was able to differentiate between natural and artificial Peru balsam because the natural product gave a much more complicated chromatogram than the artificial substance when alcoholic extracts were choromatographed on alumina.

The behavior of the zone has been described from the inception of the zone to its ultimate, or penultimate, stage: the former if it has migrated out of the column as a separate volume of solution; the latter if it remains on the adsorbent but clearly separate from preceding and following zones. In this latter case there remain the final operations: removal of the zone and elution of the adsorbed substance. These will now be dealt with briefly.

After development is complete and zones are found well separated on the column then the last of the developer liquid is allowed to drain from the adsorbent, and the cylinder of *adsorbent is extruded* from the tube. If the adsorption tube is made with a slight taper extrusion is simplified.[131] The column is then separated between the zones. If the substances on the column are sensitive to oxygen then the liquid which has drained out must be replaced with some inert gas. In any case enough liquid must be removed from the column so that when it is extruded it will retain its shape and not collapse into a sludge, for this might obscure the limits of the zones. Sometimes the adsorbent has swelled or otherwise become so tightly packed that it is difficult to extrude the column. In this case one may reach in with a rod or wire and loosen up the adsorbent in

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[129] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography,* Wiley, New York, 1943; H. H. Strain, *Chromatographic Adsorption Analysis.* Interscience, New York, 1945.

[130] Valentin, *Pharm. Ztg.,* 80, 469 (1935); 81, 943 (1936); *Chem. Abstracts,* 30, 8522 (1936).

[131] Georges, Bower, and Wolfrom, *J. Am. Chem. Soc.,* 68, 2169 (1946), obtained tapered tubes from the Scientific Glass Apparatus Co., Bloomfield, N. J. (see footnote 5 in this article.)

portions, shaking or flushing each out; or the tube may cut up. A segmented tube has been designed for easy removal of the adsorbent.[132]

The adsorbent comprising the zone, and often some adsorbent at each end of it, is now *eluted.* The most effective way to bring about elution is to place the material loosely in a Tswett tube and pass the eluent solution down through it. This consumes the least amount of eluent. Otherwise, the material may be shaken in a flask with the eluent and then filtered from it. Since filtration is necessary in any case (except in a few, where decantation is sufficient) it is as well to carry out the elution in the manner suggested above, which accomplishes filtration at the same time.

The *eluent solution* should have the following characteristics: it should be a good solvent for the substance to be eluted; it should be or should contain a substance more strongly adsorbed than that to be eluted; and it should be easily separated from the substance. If the eluent is a good solvent it will by this fact aid in desorbing the adsorbed substance. If in addition it contains some molecule which will displace the adsorbed substance, then its efficiency will be increased.

The removal of the adsorbed substance can sometimes be accomplished very easily by dissolving the adsorbent.[133] Thus Graff and Skau[134] recovered fatty acids from zones on magnesium oxide by dissolving the adsorbent in concentrated hydrochloric acid and extracting the fatty acid with ether.

In an alternative procedure which has already been mentioned the column containing the adsorbate is treated with a graded series of eluent solutions of increasing strength to wash out the various components of the mixture more or less selectively (see Chapter V).

A word or two may be said concerning the *instrumentation* of chromatography. A number of instruments have been contrived for recognizing and helping to separate zones as well as for quantitative estimation of the amounts of adsorbed substances in the zones. As Tiselius and Claesson[135] have pointed out, the most generally useful instrument for recognizing the concentration changes in liquid chromatograms are optical instruments, particularly those which measure refractive index. In special cases one may use a colorimeter, or a spectrograph, perhaps a continuously recording one. With acids in the appropriate media one might use a *p*H meter; with ionizable substances one might use conductivity measurements; or measurement of dielectric change might be used, etc. (see above).

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[132] Békésy, *Biochem. Z.*, 312, 100 (1942).

[133] Duschinsky and Lederer, *Bull. soc. chim. biol.*, 17, 1534 (1935).

[134] Graff and Skau, *Ind. Eng. Chem., Anal. Ed.*, 15, 340 (1943).

[135] Tiselius and Claesson, *Arkiv Kemi, Mineral. Geol.*, **B15**, No. 18 (1942).

The most throughly worked out methods have been reported by Tiselius and Claesson.[135,136] Tiselius used the Toeppler schlieren method in conjunction with frontal analysis, as mentioned above. Where this is applicable the recording and other devices which improve the method, and which have been so useful in studies on electrophoresis, may be applied.

With Tiselius, Claesson has developed an interferometric method for following the development, and Claesson[136] has contrived for this a self-recording instrument. Dutton[137] also developed an instrument in which interferometry is used. It may be expected that when rugged instruments of these kinds become available chromatography will become much more widely used.

Although interferometry is generally useful there are analyses for which it may not be the method of choice. An example is the analysis of amino acids. Moore and Stein[138] found the sensitivity of their colorimetric ninhydrin method, which is 1 part per million of amino acid in aqueous or alcoholic solution, to be about 150 times that of refractometric measurement to 2×10^{-5} n_D.[139]

VI. ADVANTAGES AND LIMITATIONS OF CHROMATOGRAPHY

The advantages and limitations of chromatography in comparison with other separation processes need some discussion. The advantages will be considered first, and a brief and very general comparison made with two common separation processes: distillation and solvent partition.[140] Fractional crystallization and sublimation and chemical separations will not be considered because they do not usually compete with chromatography. They usually have a different range of application.

Chromatography has advantages over distillation on several counts. Even for difficult separations the former method still uses effectively the simplest apparatus, whereas the latter requires rather complicated equipment. Again, chromatography is applicable to substances which cannot be distilled because of their inherent instability toward increased temperature or because they have no boiling point within a feasible temperature range. The low temperature at which chromatography will operate effectively is one of the greatest assets of the method. It is difficult to compare the two methods with respect to time required for given separations, since this varies so with the substances being separated. It is also difficult to compare the utility of the two methods with respect to the handling of large-scale separations. Examples could be found to support any extreme position taken in this matter. Distillation processes have a great advantage over chromatography in that the physical data upon which they may be designed are often available in the literature, easily accessible in handbooks, or else capable of intuitive prediction. They are also more familiar in the laboratory. For this reason chromatography has had the distinction of being a last-resort method unless, as in special cases (*e.g.*, with colored substances such as the carotenoids), it has already been well worked out in the application in question. The data gathered in this volume and the discussions in Chapters III and IV may help to make chromatography more useful.

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[136] Claesson, *Arkiv Kemi, Mineral. Geol.*, **A23**, No. 1 (1946).

[137] Dutton, *J. Phys. Chem.*, **48**, 179 (1944).

[138] Stein and Moore, *J. Biol. Chem.*, **176**, 337 (1948); **178**, 79 (1949); Moore and Stein, *ibid.*, **176**, 367 (1948); **178**, 53 (1949). Fraction collectors capable of gathering large numbers of successive samples of percolate are advertised by American Instrument Co., Microchemical Specialties Co., Shandon Scientific Co. (London), and Technicon Chromatography Corp.

[139] Moore and Stein, *Ann. N. Y. Acad. Sci.*, **49**, 265 (1948).

[140] Cassidy, *J. Chem. Ed.*, **23**, 427 (1946); **27**, 241 (1950).

Liquid–liquid partition processes bear to chromatography many likenesses in their advantages. Both methods may operate at low temperatures and both may thus be used to separate substances unstable to temperature rise or substances which are not distillable. Liquid–liquid extractions may use very simple apparatus and yet yield quite extraordinary separations. In this connection may be cited the work of Martin and Synge[141] and their collaborators in "partition chromatography," which seems to rely to some extent on liquid–liquid partition (see Chapter X). The work of Craig,[142] who has developed ingenious machines for countercurrent partitions, has shown how very efficient this method can be and how little material can be handled quantitatively by it. Some of his apparatus would, however, appear to be rather complicated. He has shown that a set of separatory funnels, while less convenient than the machines, will give all the necessary data. Many other countercurrent liquid–liquid partition arrangements have been devised besides these[143,141] and it is difficult to judge their place in the scheme of separation methods in comparison with chromatography. It would seem, however, due to the fact that most liquid–liquid partition curves of concentration in one phase plotted against concentration in the other approach zero with less steep slope than adsorption isotherms, that in dealing with low concentrations of substances the chromatographic method should be more effective than the liquid–liquid partition method. The chromatographic method does, however, have two inherent disadvantages which are not shared with liquid distribution methods. These will be discussed below.

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[141] Martin and Synge, *Biochem. J.*, 35, 1358 (1941).

[142] L. C. Craig, *J. Biol. Chem.*, 155, 519 (1944). L. C. Craig and D. Craig, "Extraction and Distribution," in A. Weissberger, ed., *Technique of Organic Chemistry*, Vol. III, Interscience, New York, 1950, p. 171 ff.

[143] For example, by Cornish, Archibald, Murphy, and Evans, *Ind. Eng. Chem.*, 26, 397 (1943); Varteressian and Fenske, *ibid.*, 28, 1353 (1936); Ney and Lochte, *ibid.*, 33, 825 (1941).

Moore and Stein made a rough calculation comparing a starch "partition chromatography" column and a cascade type of liquid–liquid distribution method for separating leucine and isoleucine. The conclusion was that the column (their columns were 15 to 22.5 cm. by about 2 cm.) was achieving a separation that would require several thousand separatory funnel distributions.[144] This comparison suffers from the fact that the distribution on their columns was very probably a rather complicated mixed adsorption and liquid–liquid distribution. Berg[145] compared a countercurrent adsorption process and an oil absorption process for efficiency in retaining methane, ethane, and propane gases. The adsorption process under special conditions where the gas was dilute showed definite advantages, but the advantage disappeared as the gas became more concentrated (higher pressure). The reasons for this probably are connected with the steep slope of the adsorption isotherm at low concentrations (mentioned above) and the capacity factor which is mentioned below. Some of the data from Berg's paper are given in Table VIII-4.

One of the important advantages of chromatography over the two methods referred to above is its capacity to effect the separation of small amounts of substances from very large quantities of solvent. This has been pointed out in the monographs on chromatography.[146] Perhaps the classic example is the experiment in which Koschara[147] isolated, by concentration by batchwise adsorption followed by chemical purification and chromatography, some 17 mg. of flavin from 5000 liters of urine.

Another advantage of the chromatographic method lies in its ability to detect small traces of impurity in a substance and to give a quantitative estimation of its amount and, in favorable cases, to indicate when no more of the impurity is present in the substance being examined. This is discussed further below.

There is one disadvantage to the chromatographic method which is inherent in it because it is an adsorption method and which needs to be clearly indicated. This disadvantage lies in the possibility that substances

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[144] Moore and Stein, *Ann. N. Y. Acad. Sci.,* 49, 265 (1948).

[145] Berg, *Trans. Am. Inst. Chem. Eng.,* 42, 665 (1946).

[146] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography,* Wiley, New York, 1943; H. H. Strain, *Chromatographic Adsorption Analysis,* Interscience, New York, 1945.

[147] Koschara, *Ber.,* 67, 761 (1934); *Z. physiol. Chem.,* 229, 103 (1934).

TABLE VIII-4

Comparison of a Countercurrent Adsorption Process ("Hypersorption") and an Oil Absorption Process[145]

Hydrocarbon	Pressure, lbs. absolute	Retention, lbs./lb.		Ratio: adsorption/absorption	B.p., °F.
		Activated charcoal	Absorption oil		
Methane.......	1	0.00199	0.000022	90.5	−300
	40	0.022	0.00088	25.0	−237
Ethane.........	1	0.023	0.00027	85.0	−198
	40	0.122	0.0107	11.4	−88
Propane........	1	0.113	0.0014	80.7	−136
	40	0.200	0.055	3.6	−2

Note: The adsorbent was a granular activated coconut shell charcoal; the oil a 200 mol. wt. absorption oil; the temperature 100°F.

may undergo chemical change when in the adsorbed state or at any rate during the process of adsorption and desorption. This means that the chromatographic method may not be applied to all substances with impunity.[148] The changes which may occur upon the surfaces of adsorbents are discussed in Chapter IX. Here, only a few specific cases will be mentioned in order to emphasize this limitation. Gillam and El Ridi[149] observed that adsorbents such as alumina or calcium hydroxide could bring about isomerizations of carotene. These observations have been amplified and it has been shown that the carotenoid pigments and related substances, such as the vitamins A, can be transformed at the surfaces of various adsorbents.[150]

It has been shown that *cis* compounds may be isomerized to the *trans* forms in the case, for example, of *cis*-benzoin oxime, and *cis*-anisoin oxime, though the amount of isomerization was small.[151] Hydrolysis has been observed to occur when diacetyl toxicarol in chloroform solution was passed through a column of activated alumina.[152] Steroid esters of several kinds have been observed to undergo hydrolysis on alumina. Dasler[153] refers to several instances of this kind. Trappe[154] observed that in the presence of HCl (formed readily in the light from trichloroethylene which may be used as a solvent) free or esterified cholesterol is decomposed with a blue-red coloration when adsorbed on silica gel. Also, acid earths produced some reaction with cholesterol. Trappe observed hydrolysis of triglycerides to occur on the column of alumina under certain conditions.

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[148] Holmes and Corbet, *J. Biol. Chem.*, 127, 449 (1939).

[149] Gillam and El Ridi, *Nature*, 136, 914 (1935); *Biochem. J.*, 30, 1735 (1936); 31, 1605 (1937).

[150] Zechmeister and Tuzson, *Biochem. J.*, 32, 1305 (1938); *Ber.*, 72, 1340 (1939); Zechmeister and Schroeder, *J. Am. Chem. Soc.*, 64, 1173 (1942); Polgár and Zechmeister, *ibid.*, 64, 1856 (1942); Bauernfeind, Baumgarten, and Boruff, *Science*, 100, 316 (1944); Swain, *Fisheries Res. Board Canada, Progress Repts., Pacific Sta., No. 49*, 13 (1941); *Chem. Abstracts*, 36, 615 (1942); Meunier, *Compt. rend.*, 215, 470 (1942).

[151] Zechmeister, McNeely, and Sólyom, *J. Am. Chem. Soc.*, 64, 1922 (1942).

[152] Cahn and Phipers, *Nature*, 139, 717 (1937).

[153] Dasler, *Science*, 107, 369 (1948).

Evidence of aminolysis or even extensive oxidation of amino acids on charcoal columns was obtained by Wachtel and Cassidy.[155] Tiselius[156] showed that such reactions could be prevented by treating ("poisoning") the adsorbent with HCN.

The forces which operate in adsorption may be sufficient in some cases to decompose molecular complexes. Plattner and Pfau[157] have shown that chromatographic adsorption is a general method for decomposing molecular compounds of hydrocarbons such, for example, as the picrates.

The few instances produced above are sufficient to urge caution in the use of chromatography for the separation of labile compounds. Zechmeister has given a general discussion of this subject.[158] Further information may be found in Chapter VII.

Although this drawback to the method of chromatography may at times cause some inconvenience it need not pose an insuperable difficulty, for it is usually found that a different adsorbent or solvent will serve for the separation without causing decomposition. *The utility of the method is therefore not seriously limited in practice.* However, Gillam's warning should be heeded that care should be taken to differentiate between genuine separations and transformations caused by the adsorption process. In this connection attention may be called to an interesting case of "double zoning" observed by Schroeder.[159]

Another limitation of chromatography, inherent in the adsorption distribution is that of somewhat low capacity. This limitation is a result of the nearly two-dimensional nature of the interfacial phase. It is not a particularly serious limitation in the laboratory, and it has not prevented industrial preparative chromatography, as mentioned above. Actually, the capacities of some adsorbents can be rather high. For example, 1 g. of Darco G-60 charcoal in a small tube will retain approximately 0.2 g. lauric acid from a solution containing 1.5 g./liter (0.0075*M*) or about 0.4 g. stearic acid from a solution containing 1.54 g./liter

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[154] Trappe, *Biochem. Z.*, 306, 316 (1940); 307, 97 (1941).

[155] Wachtel and Cassidy, *J. Am. Chem. Soc.*, 65, 665 (1943).

[156] Tiselius, *Arkiv Kemi, Mineral. Geol.*, B15, No. 6 (1941).

[157] Plattner and Pfau, *Helv. Chim. Acta*, 20, 224 (1937).

[158] Zechmeister, *Ann. N. Y. Acad. Sci.*, 49, 145 (1948).

[159] Schroeder, *Ann. N. Y. Acad. Sci.*, 49, 204 (1948).

(0.0054 *M*).[160] This limitation is mentioned not because it causes much inconvenience in conventional chromatography but because it does become important in work with paper strips or sheets (Chapter X).

VII. USE IN TESTING PURITY

Chromatography has long been recognized as a powerful tool for *testing purity*. It combines the two requirements for an acute and discriminating method of testing purity[161,162]: an efficient attempt at separating the putatively pure substance into fractions, and comparison of the fractions to test their identity. In a test of purity the substance to be examined is submitted to chromatography. Any impurity will be expected to be either more or less strongly adsorbed, so that on development there will be evidence of more than one zone. With a pure substance, only one zone will form. The attempt at separation is made in the countercurrent application of the adsorption distribution; the test of identity comes since different substances would presumably be adsorbed to different extents.

TABLE VIII-5

Chromatography on Silica Gel as Test of Purity of Fatty Acids[163]

Silica gel	Acid number: Filtrate	Acid number: Eluate
Myristic Acid, m.p. 58°, Acid Number 245.8 (Theor. 245.6)		
A	236.7	260.3
E, fine-pored	247.2	248.8
E, medium-pored	243.8	248.5
E, wide-pored	232.1	258.4
Palmitic Acid, "Acid. palmitinic. purissimum"		
A	223.9	218.2
E, fine-pored	215.6	214.9
E, medium-pored	215.6	219.9
E, wide-pored	224.5	214.1

An example of the use of chromatography for testing purity was given by Kaufmann.[163] Commercial samples of "purest" myristic acid and palmitic acid were dissolved in benzene (2.5 g. acid in 10 g. benzene) and passed through small columns of silica gel, under suction, the column being rinsed with 5 g. benzene. The fitrate was collected and the solvent removed. The substance on the adsorbent was eluted with 10 g. acetone. Four different silica gels were used. The acid numbers of the eluate and filtrate were compared. They should have been identical if the acids had been pure. The data given in Table VIII-5 indicated that even these substances, which showed initially the correct acid number, contained small amounts of higher and lower acids. Cassidy[164] was able to demonstrate the presence of 0.67% ester in the presence of mixed higher fatty acids by chromatography of a petroleum ether solution on Darco G-60.

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[160] Cassidy, *J. Am. Chem. Soc.*, 63, 2735 (1941).

[161] Cassidy, *Fed. Proc.*, 7, 464 (1948).

[162] Cassidy, *J. Chem. Ed.*, 23, 427 (1946).

[163] Kaufmann, *Angew. Chem.*, 53, 98 (1940).

Barton and Jones[165] tested the homogeneity of samples of sitosterol by oxidation, followed by chromatographic analysis of the ketones present. They concluded that this method gave a more delicate and convenient criterion of purity than the usual fractional crystallization methods, and suggested that it might be generally applicable in the sterol field.

Winterstein and Stein[166] were able to detect and separate 2 mg. of dipalmityl ketone in 300 mg. of a hentriacontane which showed the theoretical analysis and a good melting point. In that laboratory, also, chromatography was used to isolate 0.05% carbazole from anthracene.[167] The purified anthracene showed the blue fluorescence which is known to be quenched by $^1/_{30,000}$% of naphthacene. The original sample of anthracene had contained 0.5% of naphthacene. Mair[168] and his co-workers at the Bureau of Standards have shown that the aromatic hydrocarbon content of a mixture of paraffins, naphthenes, and aromatics can be determined within ±0.2% through chromatography on silica gel.

The chromatographic test for purity (and other distribution tests) fails when a mixture distributes itself like a pure substance. The situation is analogous to that encountered in eutectic formation and azeotropism. An observation by Bauernfeind, Baumgarten, and Boruff[169] may furnish an example of this difficulty. They found two pigments which were chromatographically identical by mixed adsorption on alumina and development with reagent chloroform but which were not identical spectrophotometrically. The remedy in such a situation, as with other distribution tests, is to change the conditions of the test. This involves using different adsorbents and different solvents, preferably choosing these to have different polarities from those first taken.

Another phenomenon which can occur (and which is not absent from other distribution tests of purity) is in effect the reverse of this; instead of

[164] Cassidy, unpublished; see *Fed. Proc.*, 7, 464 (1948).

[165] Barton and Jones, *J. Chem. Soc.*, 1943, 599.

[166] Winterstein and Stein, *Z. physiol. Chem.*, 220, 247 (1933).

[167] Winterstein, Schön, and Vetter, *Z. physiol. Chem.*, 230, 158 (1934).

[168] Mair, *Ann. N. Y. Acad. Sci.*, 49, 218 (1948).

[169] Bauernfeind, Baumgarten, and Boruff, *Science*, 100, 316 (1944).

a mixture appearing pure, a pure substance yields more than one zone. This is not very common. Examples have been given above, the classical one being the observation by Gillam and El Ridi[170] that a pure carotenoid can be isomerized on the chromatography adsorbent, yielding, then, more than one zone. The double zoning reported by Schroeder[171] is another example of the phenomenon in which a presumably homogeneous substance appears mixed.

VIII. CHROMATOGRAPHY WITH MOBILE INTERFACES

Various investigators have indicated that separations with foams and emulsions can be carried out rather easily and efficiently in certain cases. The countercurrent use of foams and emulsions is certainly a chromatographic procedure[172] and therefore belongs in this chapter. The subject has been reviewed by Shedlovsky.[173]

1. Apparatus

The apparatus needed for foam separations can be relatively simple. There is needed a method of forming very small bubbles. The convenient procedure is to force a gas through an orifice. Schütz[174] used a replaceable capillary orifice, so that the size of opening could be varied, or a multijet with 12 to 20 openings of approximately equal diameter. Abribat[175] used a porous cup. Miles, Shedlovsky, and Ross[176] used platinum or stainless steel "spinnerettes"[177] by means of which they could obtain foams of uniform bubble size.

The orifice is mounted at the foot of a tube in which the column of foam can be formed. With solutions which differ in their ability to foam, tubes of different length and diameter are needed. The liquid to be treated is placed in this tube and the foam is produced by bubbling filtered air, nitrogen, or other gas up through the orifice. A fairly large interfacial area can be obtained. For example, Miles[178] obtained a foam of uniform bubble size by bubbling air through a single orifice. He calculated that an interfacial area of approximately 2 × 10^4 cm.^{2} was produced for about 1100 ml. of foam with bubbles of 0.017 ml. volume.

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[170] Gillam and El Ridi, *Biochem. J.*, 30, 1735 (1936).

[171] Schroeder, *Ann. N. Y. Acad. Sci.*, 49, 204 (1948).

[172] Cassidy, *Ann. N. Y. Acad. Sci.*, 49, 324 (1948).

[173] L. Shedlovsky, *Ann. N. Y. Acad. Sci.*, 49, 279 (1948).

[174] Schütz, *Trans. Faraday Soc.*, 42, 437 (1946); Bader and Schütz, *ibid.*, 42, 571 (1946).

[175] Abribat, *Compt. rend.*, 209, 244 (1939); H. Devaux, P. Woog, M. Abribat, A. Dognon, and P. Lecompte du Nouy, *Sur les phénomènes de mouillabilité et les applications de ces phénomènes*, Hermann, Paris, 1942.

[176] Miles, Shedlovsky, and Ross, *J. Phys. Chem.*, 49, 93 (1945).

[177] Obtainable from platinum fabricators and supply houses.

[178] Miles, *J. Phys. Chem.*, 49, 71 (1945).

The foam which is produced above the solution can be handled in various ways. Access to the column of foam in the tube was obtained by Abribat[175] by using a tube made up of cylindrical segments connected by sleeves, which allowed the tube to be dismantled. He, also, with small amounts of foam, used a narrow thin-walled tube which could be cut in pieces to give access to the foam. Schütz[174] used a tube which was designed so that by control of the flow of gas the foam could be carried over the top of the tube and collected. Abribat[175] also used a similar device.

The apparatus must be designed to allow time for drainage of the foam, since this may be an important feature of the separation. In addition, Miles[178] used an apparatus which could be rocked so that the bulk liquid and the foam or emulsion could be brought into gentle contact if necessary to improve the chance for steady-state distribution of adsorptive between the bulk phase and the interface. Careful horizontal stirring may also be used.[175] It would appear that the steady-state distributions studied by Miles and his co-workers[179] correspond to batchwise processes, while the fractionations of Abribat, Schütz, and others[180] are more like differential countercurrent processes (Chapter VIII). This affects the design of the apparatus.

2. Procedure

Shedlovsky[181] has pointed out that adsorption in foam is indicated as a means of separating a surface-active substance from dilute solution if the surface tension concentration curve shows a minimum. If the interfacial tension–concentration curve shows a minimum, then adsorption in an emulsion of the two phases is indicated. In each case the most effective removal would be expected at the concentration corresponding to the minimum.

In the countercurrent processes of Abribat and Schütz more than one adsorptive may be present. If there is any preferential adsorption on the foam, then at a given gas pressure and bubbling rate the foam will be stabilized largely by the preferentially adsorbed substance. The amount of this substance will control the amount of foam produced under the given conditions. As foam is formed it removes material from solution until the depleted solution can no longer form foam of this stability, at which point a more or less steady state may be reached. At this point the column of foam is removed,[182] or perhaps it has been flowing out of the apparatus up to this point.[183] The next fraction is obtained by increasing the flow of gas (increasing the pressure). It is emphasized by those who have used this method that adequate time for foam drainage is important, together with adequate chance for contact between the bubble interfaces and the bulk solution. This is explainable on the basis that the adsorption is competitive between the various species of molecules present, and adequate opportunity must be provided for the more strongly adsorbed ones to reach the surface and to displace those less strongly adsorbed which had been taken up because they were closer to the interface and their solution had been (locally) depleted of more strongly adsorbed molecules.

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[179] Miles and L. Shedlovsky, *J. Phys. Chem.*, 48, 57 (1944); Miles, *ibid.*, 49, 71 (1945); L. Shedlovsky, *Ann. N. Y. Acad. Sci.*, 46, 429 (1946).

[180] Abribat, *Compt. rend.*, 209, 244 (1939); Schütz, *Trans.-Faraday Soc.*, 38, 85, 94 (1942); 42, 437 (1946); Dognon, *Bull. soc. chim. biol.*, 23, 249 (1941); *Rev. sci.*, 79, 613 (1941); Dognon and Dumontet, *Compt. rend. soc. biol.*, 135, 884 (1941).

[181] L. Shedlovsky, *Ann. N. Y. Acad. Sci.*, 49, 279 (1948).

The authors referred to give details of the procedures used for various separations, and their papers should be consulted. Foam separation has been used with dyestuffs,[182] proteins,[182–184] fatty acids and lipoid materials,[182] saponin,[182,183] and bile acids[185] for separating mixtures of different bacteria by a process which Dognon calls "microflotation."[184] Sometimes the separated substances actually crystallize in the foam. Sensitive proteins such as globulins[184] may be denatured in the foam.

The process of foam fractionation may be carried out in the hot or cold by the use of jacketed columns. It has been used in large-scale as well as in small-scale operations. Although this discussion has been largely restricted to the separation of substances of molecular and micellar dimensions materials of larger particle size can be handled, such as bacteria (see above). If the particle size of the substances being separated is sufficiently large, one enters the field of ore and other flotations.

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[182] Dubrisay, *Chimie & industrie,* Special No. 1045 (June, 1933); *Chem. Abstracts,* **28,** 353 (1934); *IX Congr. intern. quím. pura y aplicada,* **2,** 375 (1934); *Chem. Abstracts,* **29,** 7151 (1935); Abribat, *Compt. rend.,* **209,** 244 (1939); H. Devaux, P. Woog, M. Abribat, A. Dognon, and P. Lecompte du Nouy, *Sur les phénomènes de mouillabilité et les applications de ces phénomènes,* Hermann, Paris, 1942.

[183] Schütz, *Trans. Faraday Soc.,* **38,** 85, 94 (1942); **42,** 437 (1946).

[184] Dognon, *Bull. soc. chim. biol.,* **23,** 249 (1941); *Rev. sci.,* **79,** 613 (1941); *Chem. Abstracts,* **38,** 2979 (1944); H. Devaux, P. Woog, M. Abribat, A. Dognon, and P. Lecompte du Nouy, *Sur les phénomènes de mouillabilité et les applications de ces phénomènes,* Hermann, Paris, 1942; Dognon and Dumontet, *Compt. rend. soc. biol.,* **135,** 884 (1941); see also Elkes, Frazer, Schulman, and Stewart, *Proc. Roy. Soc. London,* **A184,** 102 (1945).

[185] Bader and Schütz, *Trans. Faraday Soc.,* **42,** 571 (1946).

IX. APPLICATIONS OF CHROMATOGRAPHY

The applications and possible applications of chromatography are far too numerous to list here. Excellent collections and lists are already availabe in the books by Zechmeister and Cholnoky,[186] Strain,[187] Williams,[188] and others. Strain and Harris have brought the listing further up to date.[189] As far as possible applications are concerned, every listing of relative adsorbability in this volume implies probable chromatographic separability.

The technique of chromatography, its application and its theory, are in a state of active development. The useful technique of displacement analysis, described above, appears to have been given greater precision by Tiselius and Hagdahl's method of carrier displacement.[190] In this method, the mixture to be separated (it can be quite small in quantity) is mixed with a convenient amount of "carrier" easily separable from it. The carrier contains a number of substances the adsorption isotherms of which lie intermediate between those of the components of the mixture so that essentially each small "step" of component of the mixture (Fig. VIII-14) is preceded by a "step" of carrier substance. Thus the components of the mixture are spaced out, and the zones, even when very small, can be separated relatively easily. An example of this method is given by Holman,[191] who uses as carrier substances the methyl esters of the fatty acids contained in the mixture to be separated. The method of carrier displacement is reminiscent, in principle, of the "amplified"[192] and carrier[193] distillation techniques. The interferometric instrument of Tiselius and Claesson[194] appears to have been made more useful by widening its concentration range using the technique of "crossing over."[195] Essen-

[186] L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography*. Wiley, New York, 1943. L. Zechmeister, *Progress in Chromatography 1938–1947*, Chapman & Hall, London, 1950.

[187] H. H. Strain, *Chromatographic Adsorption Analysis*. Interscience, N. Y., 1945.

[188] T. I. Williams, *An Introduction to Chromatography*. Chemical Pub. Co., Brooklyn, 1946.

[189] Strain, *Anal. Chem.*, **21**, 75 (1949); **22**, 41 (1950). Harris, *Ind. Eng. Chem.*, **42**, 20 (1950).

[190] Tiselius and Hagdahl, *Acta Chem. Scand.*, **4**, 394 (1950).

[191] Holman, presented at the 118th meeting of the American Chemical Society, Chicago, Sept., 1950.

[192] Bratton, Felsing, and Bailey, *Ind. Eng. Chem.*, **28**, 424 (1936); Axe and Bratton, *J. Am. Chem. Soc.*, **59**, 1424 (1937).

[193] Hickman, *Ind. Eng. Chem.*, **29**, 968 (1937).

[194] Tiselius and Claesson, *Arkiv Kemi, Mineral. Geol.*, **B15**, No. 18 (1942); Claesson, *ibid.*, **A23**, No. 1, 1946.

[195] Holman, *Anal. Chem.*, **22**, 832 (1950).

tially, this technique allows the solution in the reference cell of the interferometer to be increased in concentration in a known way during the course of an analysis, so that at a point in the analysis a new base line of refractive index can be set up.

Kirchner and co-workers[196] have developed a "chromatostrip" and "chromatobar" technique which may make possible improved standardization of technique particularly in the preparation of the column. Adsorbent is bonded with starch, plaster of Paris, or other agent, and spread uniformly on a glass plate. This is dried carefully. The resulting "chromatostrip" may be used in lieu of a chromatographic column. The mixture to be separated is applied as a zone across the strip near one end, and the strip is stood in a closed jar so that it rests on a wad of cotton in a layer of developer solvent. Upward development is used (see Chap. X, Section IV-2). The "chromatobar" is a rod of adsorbent, bonded as above, and cast in a suitable shape and length around an axially placed glass rod support. Upward development is also used, with a special distributor to spread the developer uniformly to the base of the column. The strips and columns were used by the authors to separate terpenes. A list of streak reagents for chromatography has been published.[197]

Ever since the early days of adsorption, attempts have been made to relate extent of adsorption to chemical structure of the adsorptive (Chapter IV). The advent of chromatography gave more urgency to these attempts, and much work has been done in the direction of relating sequence of zones on the column, as well as rate of movement of zones, to the chemical nature of the adsorptive in the zone. A fresh approach to this problem has been taken by LeRosen and co-workers.[198] The chemical structure of the adsorptive, adsorbent, and developer in a given case, and as a first approximation, controls the adsorption distribution, and hence the rate of movement of a zone relative to that of the developer solution (that is, controls the R value). Further, the interfacial activity of an adsorptive is, also as a first approximation, a summation of the interfacial activities of the various functional groups present. This is an application of Langmuir's *principle of independent surface action.*[199] LeRosen and his group have attempted to evaluate these functional group interactions. They have classified the types of interactions which may lead to adsorption into those involving electron donation, electron acceptance, and hydrogen bond formation. The evaluation is made to take into account the

[196] Kirchner, Miller, and Keller, and Miller and Kirchner; in press, personal communication.

[197] LeRosen, Monaghan, Rivet, Smith, and Suter, *Anal. Chem.*, 22, 809 (1950).

[198] LeRosen, Monaghan, Rivet, and Smith, in press; personal communication.

[199] Langmuir, *Colloid Symposium Monograph,* 3, 48 (1925). See p. 316.

interaction properties of the adsorbent, developer and adsorptive. Assuming certain values, the authors calculated others. This promising investigation gives evidence that if other factors (of a geometrical nature, for example) can also be evaluated, a basis will be obtained for the selection of adsorbents for given separations, and for the choice of developer. The authors have also used this approach to characterize adsorbents.[200]

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[200] Monaghan, Suter, and LeRosen, *Anal. Chem.*, 22, 811 (1950).

CHAPTER IX

Ion Exchange Methods

I. INTRODUCTION

Ion exchange operates through the competitive distribution of ion species between a bulk phase and an interface: an adsorption process. In some cases, however, there is evidence that there is also a sorption of the adsorptive into the exchanger. Ion exchangers are insoluble substances which bind ions in such a way that the ions may be easily and reversibly replaced by others from solution in contact with the exchanger. Ion exchange phenomena have been recognized for a long time. The early work was principally concerned with the implications of ion exchange for soil chemistry, and this has continued to be an important field for investigation. The colloidal ion exchangers such as clays (Chapter VII) and sols of various kinds[1] will not be discussed here.

The study of ion exchange was greatly stimulated by the production of synthetic zeolites which not only allowed further controlled investigation, but also extended the industrial applications of these substances. An additional stimulus was provided by the development of the synthetic organic exchangers which followed on the inventions of Holmes and Adams,[2] for this allowed the production of ion exchangers of relatively homogeneous functional types, of wide stability ranges, and of different exchange potentials.[3]

The ion exchangers are all polymeric or macromolecular substances. They are insoluble in ordinarily used (*i.e.*, aqueous) solutions, and thus serve to immobilize the ions which they bind. They can be classified under the headings inorganic and organic exchangers. This is a convenient practical classification because the two types of exchangers differ in many ways, especially as regards stability toward strong acids and bases. This classification may have to be discarded in favor of one with a basis more fundamentally related to the exchange process when more is known about these substances. The inorganic ion exchangers are mostly crystalline substances, the organic exchangers being less ordered in their structure.[4]

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[1] Bolam and Duncan, *J. Chem. Soc.*, 1936, 1317.

[2] Adams and E. L. Holmes, *J. Soc. Chem. Ind.*, 54, 1T (1935).

[3] R. J. Myers, in Kraemer, ed., *Advances in Colloid Science*, Vol. I, Interscience, New York, 1942, p. 317; Kunin, *Anal. Chem.*, 21, 87 (1949).

[4] Zachariasen and Mooney—from Boyd, Schubert, and Adamson, *J. Am. Chem. Soc.*, 69, 2818 (1947). See footnote 8.

In each classification the exchangers can be divided into anion and cation exchangers; however, some substances are capable of either anion or cation exchange depending on their pretreatment and the *pH* of the medium. A classification of exchangers is given in connection with the discussion of clays in Chapter VII.

This section does not pretend to an encyclopedic treatment of ion exchange substances. A number of review articles and books are available.[5] What is intended is to present a systematic, more or less homogeneous introduction to those aspects of the subject which seem germane to this book. It would in any case be impractical to describe and refer to all the work which has probably been done in this field.

II. ION EXCHANGE SUBSTANCES

Table IX-1 contains a list of ion exchangers, their compositions, capacities such as are known, and sources. An endeavor has been made to include all exchangers, but the number is continually changing, and information about the nature of the exchangers is sometimes difficult to obtain. This table does not include such materials as may be prepared for special purposes. For example, McIntire and Schenck[6] prepared a carboxylic exchanger by *partial* esterification of cotton with succinic acid and other dibasic acids, one carboxyl group of which could remain free. They obtained, in one case, a cotton succinate with a sodium ion binding capacity of 3.15 meq./g.

TABLE IX-1

Names, Compositions, Capacities, and Sources of Ion Exchangers*

Name	Type	Total capacity meq./g.	Total capacity meq./ml.	Sources†
	Inorganic Cation Exchangers‡			
Crystalite	synthetic aluminosilicate	—	—	*a*
Decalso	synthetic zeolite	—	—	*b*
Doucil	synthetic zeolite	—	—	*c*
Glauconite	greensand, aluminosilicate	0.18–0.2	—	—
Nalcolite	synthetic zeolite	—	—	*d*
Permutit	synthetic zeolite	1.0–3.0	—	*b*
Verdite	a greensand	—	—	*a*
Zeo-Dur (2 types)	a greensand	—	—	*b*

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[5] Griessbach, *Angew. Chem.*, 52, 215 (1939); Block, *Chem. Revs.*, 38, 501 (1946); Tiselius, *Advances in Protein Chem.*, 3, 67 (1947); Applezweig, *Ann. N. Y. Acad. Sci.*, 49, 295 (1948); Kunin, *Anal. Chem.*, 21, 87 (1949); 22, 64 (1950); Winters and Kunin, *Ind. Eng. Chem.*, 41, 460 (1949); F. C. Nachod, ed., *Ion Exchange Theory and Application*, Academic Press, New York, 1949; R. Kunin and R. J. Myers, *Ion Exchange Resins*, Wiley, New York.

[6] McIntire and Schenck, *J. Am. Chem. Soc.*, 70, 1193 (1948).

TABLE IX-1. *Continued*

Name	Type	Total capacity meq./g.	Total capacity meq./ml.	Sources†
	Inorganic Anion Exchangers			
Hydroxyapatite	used as a fluoride exchanger	—	—	—
	Organic Cation Exchangers			
Amberlite IR-100	phenolic methylene sulfonic	1.75	0.65	*e*
Amberlite IR-105	" " "	2.70	1.00	*e*
Amberlite IR-120	nuclear sulfonic	4.20	2.15	*e*
Amberlite IR-C-50	carboxylic	10.0	4.20	*e*
Dowex 30	phenolic methylene sulfonic	4.00	1.35	*f*
Dowex 50	nuclear sulfonic	4.25	2.20	*f*
Duolite C-3	phenolic methylene sulfonic	3.25	1.00	*g*
Duolite C-20	nuclear sulfonic	—	—	*g*
Duolite CS-100	carboxylic	3.85	1.11	*g*
Ionac C-200	phenolic methylene sulfonic	2.70	0.81	*h*
Nalcite-MX	phenolic methylene sulfonic	3.00	1.15	*d*
Nalcite-HCR	nuclear sulfonic	4.15	2.10	*d*
Permutit Q	sulfonated styrene type	—	—	*b*
Permutit 216	carboxylic	5.30	1.70	*b*
Wofatit P	phenolic methylene sulfonic	1.35	0.53	*i*
Wofatit K	" " "	2.50	1.00	*i*
Wofatit KS	" " "	2.45	0.90	*i*
Wofatit C	carboxylic	7.00	2.50	*i*
Zeo-Karb	sulfonated coal	1.62	0.60	*b*
Zeo-Rex	phenolic methylene sulfonic	2.70	0.89	*b*
	Organic Anion Exchangers. Acid Adsorbers			
Amberlite IR-4B	weak base	10.0	2.50	*e*
Amberlite IRA-400	strong base	2.3	1.00	*e*
De-Acidite	weak base	9.3	1.5	*b*
Duolite A-1 to 9	weak bases (Duolite A-2)	7.0	1.20	*g*
Duolite A-40	strong base	—	—	*g*
Ionac A-300	intermediate base	7.4	1.50	*h*
Wofatit M	weak base	—	1.20	*i*
Permutit S	strong base	—	—	*b*

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* The table has been compiled from the industrial literature; the capacities and some other information are from Kunin, *Anal. Chem.*, 21, 87 (1949), Table 1, p. 89.

† Sources: *a*, Infilco Incorporated, Chicago, Ill.; *b*, The Permutit Co., New York, N.Y.; *c*, American Doucil Co., Philadelphia, Pa.; *d*, National Aluminate Corp., Chicago, Ill.; *e*, Resinous Products & Chemical Co., Philadelphia, Pa.; *f*, Dow Chemical Co., Midland, Mich.; *g*, Chemical Process Co., San Francisco, Cal.; *h*, American Cyanamid Co., New York, N.Y.; *i*, I. G. Farbenindustrie A.G.

‡ Clays are not included in this table. Professor Jenny has pointed out (*personal communication*) that clays may have relatively high capacities as exchangers. For example, a Utah bentonite showed a capacity of 1 meq. per g. [Jenny, Nielsen, Coleman and Williams, *Science*, 112, 164 (1950)]. The particles are so small, however, that percolation through beds of these exchangers is extremely slow, and they are not at present of practical chromatographic use.

III. TYPES OF EXCHANGE BEHAVIOR

Cation exchangers are of two general types: the zeolites and certain related substances which are inorganic exchangers, and the organic synthetic resins and carbonaceous exchangers. The exchange behavior of the cation exchangers may be generalized into the relation:

$$A^- M_1^+ + M_2^+ \rightleftharpoons A^- M_2^+ + M_1^+$$

where M_1^+ and M_2^+ are exchangeable cations and A^- is a portion of the exchanger mass containing a functional group. The functional groups which submit to cation exchange can be of any anionic type which can be incorporated into a polymeric, insoluble structure. The following types of functional groups are found in exchangers: $-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}^-\ \mathrm{Na}^+$ in the sodium form of a zeolite; $-\overset{}{\underset{|}{\mathrm{Al}}}-\mathrm{O}^-\ \mathrm{Na}^+$ in the sodium form of a zeolite, or in alumina treated with sodium hydroxide; $-\mathrm{SO}_3^-\ \mathrm{H}^+$ in the acid forms of sulfonated coal or lignite, or in sulfonic acid resins; $-\mathrm{CO}_2^-\ \mathrm{H}^+$ in the acid form of carboxylic acid resins; $-\mathrm{O}^-\ \mathrm{H}^+$ (phenolic) in the acid form of phenolic resins. The cation exchangers have been classed into two groups only because of differences in stability; the inorganic exchangers are not, on the whole, as stable to high and to low hydrogen ion concentrations as are the organic resins. Some of the zeolites and organic resins show high exchange capacities.

The anion exchangers can also be divided into these two classes. Their behavior may be generalized as:

$$B^+A_1^- + \mathrm{A}_2^- \rightleftharpoons B^+A_2^- + A_1^+$$

where A_1^- and A_2^- are exchangeable anions, and B^+ a portion of the exchanger containing a functional group.

The organic anion exchangers rely on primary, secondary, or tertiary amine, or quaternary ammonium functional groups for the exchange. The first three types show the same mechanism for the exchange: in a proton-donating medium (aqueous solutions) the ammonium ion forms:

$$-\overset{|}{\underset{|}{\mathrm{N}}}\!: + \overset{\mathrm{H}^+}{\mathrm{HOH}} \rightleftharpoons -\overset{|_+}{\underset{|}{\mathrm{N}}}\!:\mathrm{H} + \mathrm{HOH}$$

This then can bind an exchangeable anion. The quaternary ammonium type is set in the ammonium form, and cannot undergo this type of equilibrium with an uncharged form.

The relative position of the exchange equilibrium for inorganic cations with the same number of charges is governed to a considerable extent by the size of the ion (the hydrated radius in the solution) which, together with the charge, influence the electrostatic properties of the ion and largely determine the free energy of adsorption. Boyd, Schubert, and Adamson[7] point out that when ions of roughly the same size and with the same electron structure are compared (for example Cs^+, Ba^{+2}, and La^{+3}, which possess the electron structure of xenon) the ionic charge plays a determining role in the extent of adsorption, the adsorbability increasing from cesium to lanthanum. For ions of the same charge and analogous electron structure ionic size plays the dominant role, though other factors such as electron configuration probably have some influence. These authors use activity coefficient – concentration plots as an empirical guide to the sequence of adsorption of ions, arriving thus at the following orders of adsorption from aqueous solutions. $Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$; $< Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$; $Al^{+3} < Sc^{+3} < Y^{+3} < Eu^{+3} < Sm^{+3} < Nd^{+3} < Pr^{+3} < Ce^{+3} < La^{+3}$. Experimental measurements are correlated with the following order of adsorption affinity: $Li^+ < H^+ < Na^+ < K^+ < Rb^+ < Cs^+ << Ba^{+2} << Y^{+3} < La^{+3}$. The sequence of decreasing relative adsorbability among the rare earths has been given by Ketelle and Boyd[8] and is in the same order as that of the crystal ionic radii, and of predicted basicity, stronger bases being better adsorbed than weaker bases.

The orders of adsorption for anions on the resin Amberlite IR-4B are given by Kunin and Myers as follows:[9]

Inorganic acids at a given *p*H: $HCl < HNO_3 < H_2SO_4 < H_3PO_4$.

Organic acids at a given *p*H, but with some deviations from this general order at lower *p*H: benzoic < oxalic < formic < acetic < citric < salicylic.

Order of relative exchange abilities of anions (studied as the sodium, potassium or ammonium salts): fluoride < chloride < bromide = iodide = acetate < molybdate < phosphate < arsenate < nitrate < tartrate < citrate < chromate < sulfate.

As yet no such clear correlations between charge and ion size as are found for inorganic cations seem to have been found for anions. This is probably because of lack of information, not only regarding the relevant properties of the anions themselves, but regarding the mechanism of the exchange process. For example, it is thought by some workers that the process in aqueous solution is one of actual exchange.[10] Thus, Kunin and Myers write, for the reaction of an amine resin, an equation of the following type:

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[7] Boyd, Schubert, and Adamson, *J. Am. Chem. Soc.*, 69, 2818 (1947).

[8] Ketelle and Boyd, *J. Am. Chem. Soc.*, 69, 2800 (1947).

[9] Kunin and R. J. Myers, *J. Am. Chem. Soc.*, 69, 2874 (1947).

[10] Griessbach, *Angew. Chem.*, 52, 215 (1939); Jenny, *J. Colloid Sci.*, 1, 33 (1946); Sussman, Nachod, and Wood, *Ind. Eng. Chem.*, 37, 618 (1945); Kunin and R. J. Myers, *J. Am. Chem. Soc.*, 69, 2874 (1947).

$$RNH_2 + H_3O^+ + OH^- \rightleftharpoons RNH_2(H_3O)^+ + OH^-$$

With an acid such as HCl the reaction with the resin is conceived, then, to occur in two steps:

$$(1)\quad [RNH_2(H_3O)^+ + OH^-] + Cl^- \rightleftharpoons [RNH_2(H_3O)^+ + Cl^-] + OH^-$$
$$(2)\quad OH^- + H_3O^+ \rightarrow 2H_2O$$

Others[11] conceive the reaction as one of molecular or covalent adsorption, rather than exchange. It may be that these two types of behavior are not incompatible, and under some circumstances are indistinguishable. Certainly the lack of correlation between extent of ionization and extent of adsorption noticed by Kunin and Myers[9] argues against a pure exchange. The situation may be clarified by considering the amine resins as weak bases which are insoluble but which expose to the solution a very large "surface." In this surface are the basic groups, essentially $-\overset{|}{\underset{|}{N}}:$, which compete for protons with the other bases in the ambient medium, setting up, in aqueous solution, equilibria of the types:

$RN: + H^+ \rightleftharpoons RN{:}H^+$ ammonium formation
$HOH + H^+ \rightleftharpoons H{:}\underset{H}{O}{:}H^+$ hydronium formation
$OH^- + H^+ \rightleftharpoons H{:}O{:}H$ neutralization
$M^+A^- + H^+ \rightleftharpoons AH + M^+$ "neutralization"

Depending on the *p*H, then, reactions with the resin may take predominantly one or the other of the following forms:

$$RN: + H_3O^+ \rightleftharpoons RN{:}H^+ + H_2O = [RNH^+\ OH_2]$$
$$RN: + H_2O \rightleftharpoons RN{:}H^+ + OH^- = [RNH^+\ OH^-]$$
$$RN: + HA \rightleftharpoons RN{:}H^+ + A^- = [RNH^+\ A^-]$$
$$RN{:}H^+\ A_1^- + A_2^- \rightleftharpoons RN{:}H^+\ A_2^- + A_1^-$$

Here the symbols in brackets indicate a structure which includes the surface of the insoluble resin and an interfacial region in the solution phase near this surface. The quaternary ammonium resins would seem to operate by exchange.

IV. TYPES OF BEHAVIOR OTHER THAN EXCHANGE

The exchange polymers show behaviors other than ion exchange which occur because of their large surfaces (often highly developed internal porosities) and chemical natures. These behaviors include nonexchange adsorptions, occlusions, and dissolutions, as well as actual chemical reactions.

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[11] Schwartz, Edwards, and Boudreaux, *Ind. Eng. Chem.*, 32, 1462 (1940); Cleaver, Hardy, and Cassidy, *J. Am. Chem. Soc.*, 67, 1343 (1945); Bishop, *J. Phys. Chem.*, 50, 6 (1946).

Nonexchange adsorptions are those in which the resin takes up on its surface neutral, nonionizing molecules. Such adsorptions are often difficult to distinguish from occlusions and dissolutions, and perhaps all three types of behavior should be treated under the heading of sorption. However, the appearance of a difference will be preserved here for the sake of emphasizing its possible existence.

Occlusion by zeolites has been the subject of numerous studies.[12] The term *occlusion* is used to describe a filling up of the pores of the zeolite by solvent and solute molecules, usually without the occurrence of exchange. Thus the very porous zeolites can take up large quantities of gases. Barrer has divided these zeolites into three classes on the basis of their sieve properties, *i.e.*, their abilities to exclude molecules with a given or larger critical cross section and to occlude molecules with smaller cross sections. The classes given by Barrer are listed below.[13] For classification the zeolite is thoroughly but not severely outgassed, and its particle size should approximate 200-mesh.

Class I minerals, of which chabazite is an example, occlude *n*-paraffins such as propane and butane slowly at room temperature; occlude methane, ethane, and molecules of smaller cross section rapidly; and exclude isoparaffins.

Class II minerals, of which mordenite is an example, occlude methane and ethane slowly at room temperature, and nitrogen and smaller molecules rapidly; and exclude *n*- and isoparaffins above ethane.

Class III minerals, of which certain synthetic zeolites prepared from mordenite are examples, occlude oxygen, nitrogen, and smaller molecules at room temperature, and exclude, or virtually exclude, methane, ethane, and higher paraffins.

The occlusion, or molecular sieve, properties of zeolites were utilized by Barrer to separate mixtures of gases and of liquids. For example, in one experiment 2.0 cc. of a mixture of 20.7% *n*-heptane and 79.3% toluene was exposed to 6.0 g. chabazite in a sealed tube at 200° for 48 hrs. The *n*-heptane was quantitatively removed from the mixture by occlusion in the zeolite, while of 1.586 cc. toluene originally present 1.560 cc. was recovered. A number of such separations have been listed by Barrer and his co-workers, the applications involving such separations as ethane from propane in a flowing system at room temperature; polar molecules from their mixtures; etc. It is suggested that these zeolites may be used to break azeotropes, to dry organic vapors or liquids, and to remove small amounts of unwanted components from mixtures which have been partially purified by other processes. The utilization of the zeolites showed certain limitations, such as difficulties of recovery of the occluded substances in certain cases, polymerizations, and other reactions on, and in, the zeolite.

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[12] McBain, *Kolloid-Z.*, 40, 1 (1926); J. W. McBain, *Sorption of Gases and Vapours by Solids*, Routledge, London, 1932; Barrer, *Trans. Faraday Soc.*, 40, 374, 555 (1944); *J. Soc. Chem. Ind.*, 64, 130T, 133T (1945).

[13] Barrer and Belchetz, *J. Soc. Chem. Ind.*, 64, 131T (1945).

Organic polymers give some evidence of taking up certain substances by a process of dissolution in the body of the polymer. An example of this was noticed by Cleaver.[14] He found that a number of amino acids were sorbed by cation exchange materials at *p*H values at which very small amounts of the amino acids could be in the cationic form; furthermore, amino acids with essentially the same isoelectric point were taken up to different extents, whence the conclusion seemed to be that the sorption was not of an ionic type. Englis and Fiess[15] had reported adsorptions on exchange resins showing the order glycine $<$ leucine $<$ phenylalanine $<$ tryptophane. Cleaver observed that this was the same order in which the amino acids distributed themselves from aqueous solution into an organic phase,[16] the neutral amino acids passing into the organic phase to a greater extent as the hydrocarbon portion of the molecule increased in size ond aromaticity. He proposed the hypothesis that these neutral amino acids dissolved in the resin. Tests with alanine, norleucine, and phenylalanine supported this hypothesis, on the whole. A further correlation appeared when he showed that the extent of the sorption of norleucine and of phenylalanine in cation exchangers followed the order of equivalent weights of the resins. It seemed, therefore, that since the resin of low equivalent weight contained more polar, hydrophilic groups per unit of mass than did the resin of high equivalent weight the latter would present more nonpolar area (or volume) for sorption of the aliphatic or aromatic nonpolar parts of the amino acids, and hence would take up per gram larger quantities of the less polar amino acids. It seemed that this phenomenon might well be encountered rather frequently with the adsorption of organic substances by these resins.

Outspoken chemical reactions may be observed when organic exchange resins are treated with oxidizing or reducing agents. These resins are usually decomposed by chlorine, bromine, and chromic acid but not by sulfuric acid, ferric iron or, at room temperature, dilute nitric acid[17]

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[14] Cleaver, *Dissertation*, Yale University, 1948.

[15] Cleaver and Cassidy, *J. Am. Chem. Soc.*, 72, 1147 (1950).

[16] Consden, Gordon, and Martin, *Biochem. J.*, 38, 224 (1944); Moore and Stein, *Ann. N. Y. Acad. Sci.*, 49, 265 (1948).

[17] Bauman, *Ind. Eng. Chem.*, 38, 46 (1946).

Frizzell[18] found that Zeo-Karb could be used for a number of quantitative analytical separations, but that, at a *p*H of 4, 0.1 *N* solutions of potassium dichromate, potassium bromate, or iodate were reduced, and iodide in KI was oxidized to iodine by the resin.

V. QUALITATIVE AND QUANTITATIVE RELATIONS IN ION EXCHANGE ACTION

Ion exchangers behave as adsorbents in the sense that, as they are insoluble substances, the exchange can occur only at the "surface" of the solid in contact with the solution. It is very probable that with some changers the polymer structure is so open that one can only speak of a surface with any meaning if it is understood that the word is used in an extreme sense. In any event, to say that ion exchangers act by exchange adsorption is *not* to imply a mechanism. There seems to be some misunderstanding of this in the literature.

The exchange reaction can be represented *in terms of* an adsorption isotherm, with its attendant equilibrium treatment of the reaction:

$$\text{substance in interface} \rightleftharpoons \text{substance in solution}$$

A plot of the relation between the amount adsorbed per unit weight of adsorbent and the concentration in a fixed volume of solution in equilibrium with this at a given temperature yields an adsorption isotherm of the usual form.[19] It should be noted that usually in this method of plotting only one of the exchanging ions is explicitly accounted for, the other ion is probably not forgotten, but is neglected. This kind of treatment is legitimate if the concentration of the ion being adsorbed, say M^+, is quite low compared to that of the other ion, so that when M^+ is adsorbed the amount of the other ion which is displaced is not enough to alter the concentration appreciably. This situation has been encountered before.

The adsorption, or exchange, process can also be investigated *in terms of* the rates of the two reactions involved in the exchange of an ion:

$$R^-M_1^+ + M_2^+ \rightleftharpoons R^-M_2^+ + M_1^+$$

The forward and the reverse reaction velocities can be examined and the kinetics of the process analyzed.[20] Such an analysis may lead to conclusions about the mechanism of the exchange. For example, Boyd and co-workers[21] (see below) have found conditions under which the rate of an exchange reaction is controlled by the velocity of diffusion inside the resin particle, and conditions under which diffusion through the immobile film about the particle is rate-determining.

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[18] Frizzell, *Ind. Eng. Chem., Anal. Ed.*, 16, 615 (1944).

[19] Wiegner, *J. Soc. Chem. Ind.*, 50, 65T (1931); Jenny, *J. Phys. Chem.*, 36, 2217 (1932); 40, 501 (1936); Marshal and Gupta, *J. Soc. Chem. Ind.*, 52, 433T (1933); Boyd, Schubert, and Adamson, *J. Am. Chem. Soc.*, 69, 2818 (1947).

[20] Vanselow, *Soil Sci.*, 33, 95 (1932); for other references, see Kunin, *Anal. Chem.*, 21, 87 (1949); 22, 64 (1950).

The exchange of ions has been treated by Mayer and Tompkins[22] *in terms of* a distribution process analogous to distillation. A distribution coefficient could be derived for the exchange, and mass law relationships applied. *In other terms,* the insoluble resin particle could be looked upon as participating in a Donnan type of partition with the ambient solution as the other phase.[23] These kinds of treatment will be discussed briefly below.

In a typical exchange experiment the solution is analyzed before addition of the exchanger and after equilibrium has been reached, the difference between the two analyses being taken to represent the amount of substance adsorbed, or sorbed. This is plotted in the usual way against the appropriate equilibrium concentration. The time required to reach equilibrium varies considerably with different types of resins and different activations. In the adsorption of arginine on a cation resin activated with 5% hydrochloric acid equilibrium was reached in about 1 hr. But when the resin was activated with sodium carbonate the exchange seemed to continue for at least 36 hrs., though the possibility of destruction of the amino acid, which would simulate adsorption, was not excluded.[24] Similar behavior has been observed in other connections.[25] The rate of approach to equilibrium is not necessarily related to the capacity of the exchanger.

The data obtained from such an experiment may be expressed in terms of the Langmuir isotherm or of the Freundlich isotherm (Chapter II). The Langmuir isotherm has been used to fit exchange data by many experimenters; however, a modification in the concept on which the isotherm was derived is required.[26] There are few or no "bare spots" on the surface of the exchanger (otherwise the particles of the adsorbent would be found to be charged), but instead each site at which exchange may occur has associated with it either the type of ion originally present in the resin or an ion obtained by exchange from the solution. The equation is written, neglecting any "bare" surface:[26]

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[21] Boyd, Adamson, and L. S. Myers, Jr., *J. Am. Chem. Soc.*, 69, 2836 (1947).

[22] Mayer and Tompkins, *J. Am. Chem. Soc.*, 69, 2866 (1947).

[23] Davis, *Soil Sci.*, 59, 379 (1945); Tompkins, Khym, and Cohn, *J. Am. Chem. Soc.*, 69, 2769 (1947); Bauman and Eichorn, *ibid.*, 69, 2830 (1947).

[24] Cleaver, Hardy, Jr., and Cassidy, *J. Am. Chem. Soc.*, 67, 1343 (1945).

[25] R. J. Myers, Eastes, and Urquhart, *Ind. Eng. Chem.*, 33, 1270 (1941).

[26] Boyd, Schubert, and Adamson, *J. Am. Chem. Soc.*, 69, 2818 (1947).

$$\left(\frac{x}{m}\right)_{A^+} = \frac{kb_1C_{A^+}}{b_1C_{A^+} + b_2C_{B^+}} = \frac{k\,(b_1/b_2)(C_{A^+}/C_{B^+})}{1 + (b_1/b_2)(C_{A^+}/C_{B^+})}$$

where $(x/m)_{A^+}$ is the quantity of ion A^+ adsorbed per unit weight of adsorbent; C_{A^+} and C_{B^+} are the respective equilibrium concentrations or activities of the ions A^+ and B^+ in solution; and b_1, b_2, and k are constants. Boyd and co-workers point out that according to this equation the amount of A^+ adsorbed must depend on the ratio of the concentrations of the ions A^+ and B^+ in solution at equilibrium and hence will be independent of the dilution (as is found by the authors for the adsorption of a number of cations on an organic exchanger). They point out also that for the case where C_{B^+} is very much larger than C_{A^+} the adsorption of A^+ becomes approximately directly proportional to C_{A^+}, while for C_{A^+} very much larger than C_{B^+} the adsorption of A^+ is nearly constant and independent of concentration. The application of the Langmuir equation is discussed and generalized by these authors. They point out that the treatment depends upon the assumptions that only one kind of exchange site is present in the surface (*i.e.*, a single type of functional group), that there is no interaction between adsorbed ions, and that no double layers are formed (*i.e.*, an adsorbed cation would not then take up an anion from solution and this another cation). It might be mentioned, in passing, that even a single functional group type may present an effectively heterogeneous exchange surface, since the relative locations of the groups—their geometry on the surface—may influence their exchange potentials.

A number of experimental and theoretical investigations have been made into the kinetic aspects of the exchange process. An example can be taken from the work of Juda and Carron.[27] These authors studied the exchange of hydrogen ion and sodium ion on four organic resins. This exchange involved the reaction:

$$R^-H^+ + Na^+ \rightleftharpoons R^-Na^+ + H^+$$

which was examined starting with the acid form of the resin R^-H^+ and treating with Na^+Cl^-, or starting with the sodium form R^-Na^+ and treating with H^+Cl^- solution. The concentration of hydrogen ions in the aqueous phase was determined experimentally; then, knowing the number of hydrogen ions and sodium ions initially available, the ratio in the exchanger phase could be deduced, assuming the ionic strength of the water phase to remain constant throughout the exchange. The equilibrium constant of the reaction:

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[27] Juda and Carron, *J. Am. Chem. Soc.*, 70, 3295 (1948).

$$\frac{C_{\text{Na}^+}\ (\text{on resin}) \times C_{\text{H}^+}\ (\text{in solution})}{C_{\text{H}^+}\ (\text{on resin}) \times C_{\text{Na}^+}\ (\text{in solution})} = K$$

was worked out on the basis of concentrations and activities; also the velocity constants for the two opposing reactions were worked out. Since the concentrations of sodium and hydrogen ions in the exchanger were not readily accessible, *relative* amounts of exchanger and solution phases were connected to the rate constants, giving a relationship which was subject to experimental test.[28]

Certain simplifying assumptions and arrangements were made in designing the theory and experiment. Interionic effects in the exchanger and solution were ignored. It was assumed that the hydrogen ion concentration in the original sodium chloride solutions before contact with the acid form of the resin was zero, and that in the sodium form of the resin used at the start of the reverse reaction it was also zero. It was assumed that the hydrochloric acid used in the reverse reaction was completely ionized. In preparing the acid form of the resins it was found that drying at 80 to 85° released acid, presumably through decomposition of the

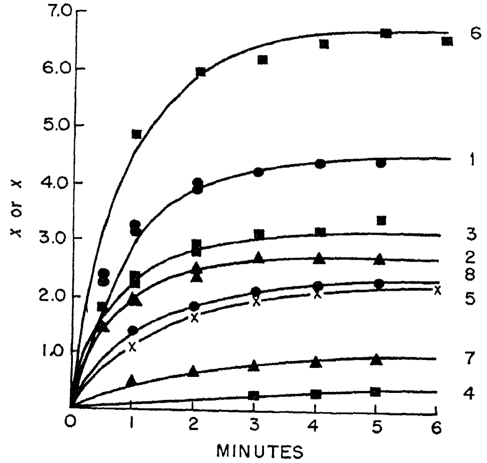

Fig. IX-1. Rate experiments on the exchange of H^+ and Na^+ on Zeo-Karb.[27] The numbers of the curves correspond to the numbered runs in Table IX-2. x is the hydrogen ion concentration in solution, in meq./liter, at the time t for the reaction $R^-H^+ + Na^+ \rightarrow R^-Na^+ + H^+$. x' is the sodium ion concentration in solution at time t for the reverse reaction.

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[28] Tompkins and Mayer, *J. Am. Chem. Soc.*, 69, 2859 (1947).

resin; therefore the resins were air dried to constant weight, and corrections (usually small) made where necessary for such hydrogen ions as were leachable from the prepared resins by distilled water. The sodium form of the resin was also air dried. Measurements of *p*H and chloride indicated that the washed, prepared resins did not release sodium ions to distilled water. The exchange capacities were determined on the basis of bone-dry resin to avoid the variable amounts of water present in air-dry material; and here, because of the decompositions observed on heating the acid form of the resin a definite temperature and duration of drying (85° for 24 hrs.) was used, with a sample of 20/40 mesh particle size.

TABLE IX-2

Data on rates for the exchange of H^+ and Na^+ on Zeo-Karb[27]

Forward Reaction: $R^-H^+ + Na^+ \rightarrow$

Run No.	a	b	x_e	k	$k_{av.}$
4	1.16	1.76	0.62	0.061–0.066	0.062
5	4.07	7.42	2.35	0.044–0.045	0.045
1	9.25	11.46	4.55	0.039–0.043	0.041
6	15.80	15.32	6.77	0.028–0.030	0.029
2	20.68	3.67	2.80	0.038–0.044	0.042

Reverse Reaction: $R^-Na^+ + H^+ \rightarrow$

Run No.	c	d	x_e	k'	$k'_{av.}$
7	1.95	2.39	1.04	0.10 –0.13	0.110
8	6.01	3.82	2.29	0.064–0.083	0.071
3	9.40	3.92	3.20	0.110–0.127	0.118

a = initial sodium ion concentration, in meq./liter; $b = 1{,}000(w_{H^+})(M)/v_{Na^+}$, where w_{H^+} is the initial weight in grams of the hydrogen form of the resin containing M milliequivalents of exchangeable ions per gram in contact with v_{Na^+} cc. of the sodium chloride solution of concentration, a; x_e = the meq. hydrogen ion exchanged at equilibrium; k = the velocity constant for the forward reaction in liters per meq. per min. c, d, x', and k' have the corresponding values for the reverse reaction, c being the initial concentration of hydrochloric acid in milliequivalents per liter.

Corrections for residual hydrogen ion in the sodium resin and sodium ion in the hydrogen resin were applied when the errors introduced by their neglect would affect the equilibrium constant by 10% or more. It was assumed that the volume of the wet exchanger phase was independent of the relative amount of sodium and hydrogen ions present in the resin, an assumption which seemed to be reasonable in this case. It was observed that the reproducibility of the data for the runs in which R^-Na^+ was reacted with H^+ were not as good as for the reverse reaction. This was laid to an attack on the resin by the concentrated salt solutions used to prepare the sodium forms. It was found unnecessary to control the temperature more closely than to 28 ± 3°. Figure IX-1 and Table IX-2 show the results of one set of experiments.

Results of the experiments on the four exchangers agreed reasonably well with a simple second-order rate equation for opposing simultaneous reversible reactions. In individual runs k and k' (Table IX-2) were usually constant to better than 20%, and were of the same order of magnitude for all four exchangers, but the values of k and k' increased with decrease in concentration, an effect laid to the dependence of the k values on the ionic strength both inside and outside of the resin particle. The ratio k/k' also agreed well with the equilibrium constant K determined separately. These measurements of Juda and Carron support the concept of the wet exchanger as a phase containing available ionized hydrogen ions which are able to diffuse to a small distance from the fixed anionic groups, and which can be displaced by other cations, the forward and reverse reactions appearing as a reversible, second-order reaction.

The mechanism of such an exchange involves diffusion of the ions inside the particle of wetted resin, diffusion through the interface between the resin phase and the solution, and the actual chemical exchange process. The mechanism was analyzed by Boyd, Adamson, and Myers[29] in order to discover which steps were rate-controling and under what conditions. The phenomena here are similar to those encountered in other distribution processes (Chapter VI), where diffusion across a stationary film, diffusion within the two phases in contact, physical interactions, and (possibly) chemical reaction are steps in the process of the distribution.

Boyd and co-workers[29] studied the exchange of a number of alkali metal cations on the resin Amberlite IR-1, using a tracer technique (radioactive sodium, rubidium, and cesium) which permitted exchange from dilute solutions of the exchanging ion. Thus in the reaction:

$$\mathrm{R}^- B^+ + A^+ \rightleftharpoons \mathrm{R}^- A^+ + B^+$$

if A^+ is present in concentration much lower than B^+, then the composition of the exchanger could be taken as essentially unchanged by the (low) adsorption of A^+, and the small amount of B^+ displaced would not, up to a point, seriously change the (high) concentration of B^+ in the solution. An improved experimental method was used which enabled the rate data to be determined under conditions of effectively constant solution concentration. This was accomplished by flowing the test solution through a thin bed[30] of the exchanger for a determined time, whereupon the exchanger was rinsed, dried with acetone, and the amount of tracer in the solid estimated by standard counting procedures.

Of the steps in the distribution process mentioned above, diffusion up to the particle boundary was eliminated as a possible rate-controlling factor by the good contact of constant composition solution with the exchanger particles obtained in the flow process. There remained to be examined the steps: diffusion of the cations and anions of the solution through the stationary interfacial film[31]; diffusion within the particle, either in channels or along the pore walls; exchange reaction at the exchange sites within the particles; diffusion of displaced cation, with anion, back out of the particle; diffusion back through the film surrounding the particle. The last two steps are the reverse of the first two.

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[29] Boyd, Adamson, and L. S. Myers, Jr., *J. Am. Chem. Soc.*, **69**, 2836 (1947).

[30] Du Domaine, Swain, and Hougen, *Ind. Eng. Chem.*, **35**, 546 (1943).

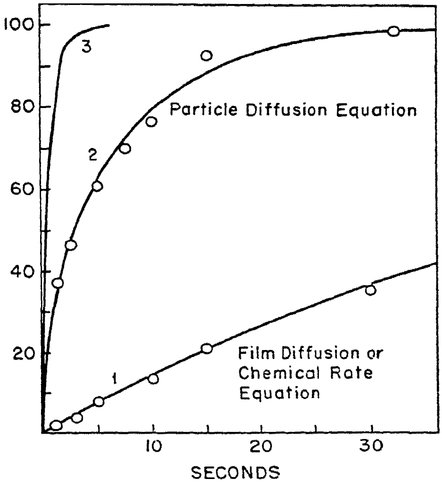

Fig. IX-2. Rate of exchange uptake of sodium ion at 30° from 0.001 *M* (curve *1*) and 0.1 *M* (curve *2*) aqueous potassium chloride solutions by 60/70 mesh Amberlite IR-1.[40] The solutions were 8×10^{-5} *M* in NaCl. The solid lines represent the best fitting theoretical curves. Curve *3* is the curve which should be fitted if boundary film diffusion (or chemical exchange) were the rate-controlling step in the 0.1 *M* solution of potassium chloride.

Equations were set up to describe the rate of each of the steps: diffusion through the stationary film bounding the particles; diffusion through the exchanger particle, with constant solution concentration; and chemical exchange (governed by mass law). It was found that the rate equations for diffusion through the stationary film and for the chemical exchange were of the same *form* and different from the equations for diffusion in the particle. Experimental determinations of the rates of exchange were tested for conformity with the equations. An example of the results is shown in Figure IX-2. The curves represent the velocities of uptake of sodium ion from 0.1 and 0.001 M KCl solutions containing 8×10^{-5} M NaCl. Evidently, in solutions of 0.1 M (or greater) concentration the diffusion within the exchanger particle is the rate-controlling process; in solutions of 0.001 M (or lower) the rate of "exchange" is controlled by the diffusion through the film enveloping the exchanger particle. Further analysis of the exchange process indicated that the diffusion constants for ions in the exchanger particle are from five- to tenfold smaller in magnitude than for the same ions in aqueous solution. Bauman and Eichorn[32] found a fivefold difference for diffusion of NaCl and HCl in Dowex-50 spheres compared with water. It was observed also that the diffusion of an ion present in small amount in solution with a large amount of another ion is speeded up if the latter has a larger diffusion constant, indicating ionic interaction.

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[31] Hunter and Nash, *J. Soc. Chem. Ind.*, 51, 285T (1932).

The implications of these and other findings are discussed by the authors. They were able to distinguish whether chemical exchange or the boundary film diffusion was the rate-controlling step in the dilute solutions by an analysis of the shapes taken by the experimental curves when particle size or film thickness (controlled by flow rate) were changed (which would affect the film-diffusion step) or when concentration and temperature (which would affect the chemical exchange rate) were changed. It was concluded that the rate of exchange was diffusion-controlled.

The Donnan concept[33] has been applied to the exchange process by a number of workers.[34] The application is based on the idea that the wet resin body in contact with solution forms a heterogeneous system between the two phases of which mobile ions can migrate but in one phase of which a nondiffusible ion exists. The situation can be shown in generalized form thus:

$$\begin{array}{ccccccc} & \textit{Resin phase} & & \qquad\qquad & & \textit{Solution phase} & \\ & M^+_1 & & & & M^+_1 & \\ R^- & & A^- & & & & A^- \\ & M^+_2 & & & & M^+_2 & \end{array}$$

According to the Donnan concept, in terms of molar activities (a), at equilibrium:

$$a_{M^+_1} a_{A^-} \text{ (in resin)} = a_{M^+_1} a_{A^-} \text{ (in solution)}$$

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[32] Bauman and Eichorn, *J. Am. Chem. Soc.*, 69, 2830 (1947).

[33] H. S. Taylor, ed., *Treatise on Physical Chemistry*, 2nd ed., Van Nostrand, New York, 1931, pp. 406, 1580.

[34] Davis, *Soil Sci.*, 59, 379 (1945); Bauman and Eichorn, *J. Am. Chem. Soc.*, 69, 2830 (1947).

and:

$$a_{M^+_2}a_{A^-} \text{ (in resin)} = a_{M^+_2}a_{A^-} \text{ (in solution)}$$

or:

$$\frac{a_{M^+_1} \text{ (in resin)}}{a_{M^+_1} \text{ (in solution)}} = \frac{a_{M^+_2} \text{ (in resin)}}{a_{M^+_2} \text{ (in solution)}}$$

For dilute solutions the equation can be written in terms of concentration (C = molar concentration):

$$\frac{C_{M^+_1} \text{ (resin)} \times C_{M^+_2} \text{ (solution)}}{C_{M^+_1} \text{ (solution)} \times C_{M^+_2} \text{ (resin)}} = K_{equil.}$$

Bauman and Eichorn tested this relation for the case of diffusion of HCl into water-wet Dowex-50 (sulfonic acid resin $RSO_3^-M^+$) in the acid form. There was no exchange, merely diffusion of H^+Cl^- into the resin. The resin decreased in volume with increase in the equilibrium concentration of acid. The concentration of HCl inside the resin particles was always lower than the equilibrium concentration outside. The Donnan relation was followed well at the higher HCl concentrations. The exchange equilibrium was also tested against the Donnan relation by immersing the hydrogen form of the resin in solutions of various cations at different normalities. The equilibrium constant K (above) held well for normalities from 0.01 to 1.0 (for the ammonium-hydrogen ion exchange, for example) but in the concentrated solutions K decreased. The authors think it quite possible that the position of the ion exchange equilibrium in this resin is determined by the difference in activity coefficients between the solution phase and the highly concentrated resin phase without involving any specific affinity of sulfonate groups for one ion over another. The mass law equilibrium relation held well also for exchange of a divalent ion on hydrogen exchanger. Rate studies led to equilibrium constants in good agreement with the $K_{equil.}$ determined by batchwise experiments.

These experiments support the conclusion that this resin (Dowex-50) when in contact with water is equivalent to a highly ionized strong salt solution. The exchanger in contact with a solution of diffusible ions takes these up to an extent and at a rate governed by the law of mass action. At equilibrium the concentration of the diffusible ions in the exchanger is then lower (Donnan effect) than that in the aqueous phase. The rate behavior suggests that for solutions of concentration above about 0.1 molal diffusion within the resin particle should be the slowest, or rate-controlling, process. These data are also supported by the work of Juda and Carron.[35]

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[35] Juda and Carron, *J. Am. Chem. Soc.*, 70, 3295 (1948).

Exchange substances have been treated as though they were solid solutions. Kielland[36] has employed this approach. The exchanger has been treated by Vanselow[37] as though it were a mixed crystal.

The fact that the data conform with a particular mathematical expression, derived on some reasonable hypothesis, perhaps with a number of simplifying suppositions, does not *necessarily* mean that the data are explained by the hypothesis and none other. This is, of course, recognized. For example, Juda and Carron[38] point out that in the exchanges which they studied a Donnan equilibrium concept[39] leads to an equilibrium relation of the same form as a base-exchange concept, and that therefore their experimental data are not adequate to make possible a decision between the two. In another case, cited above, Boyd and co-workers[40] found that a rate equation based on a chemical exchange mechanism gave an expression of the same form as an equation for the rate of diffusion through a thin film, so that no decision as to which was the rate-controlling step could be reached from a single set of rate experiments. However, in this case a decision was reached following a study of several factors which influenced the exchange, and this ruled out the chemical exchange as the rate-controlling step.

The factors that may complicate resin behavior are probably not all known or imagined. Some, however, may be listed. The existence of several types of functional groups at the interface would make the capacity of the exchanger dependent at least on *p*H if not also on specific interactions with ions. This is one of the interfacial factors which may complicate resin behavior. Probably all resins, whether chemically homogeneous or not, will on more subtle analysis show inhomogeneities related to the geometric arrangements of the functional groups. This might be so especially if several types of functional groups are present, when, for example, an *ortho* arrangement may permit a chelation which a *meta* or *para* arrangement would not allow. Or it might be so for the exchange of a polyvalent ion, which might be more tightly held through the cooperation of several functional groups suitably spaced. Other interfacial factors such as porosity may be mentioned. Resins may differ in extent of internal structure, that is, in the ratio of large to small channels, and in the presence of tapering, irregular channels of nonuniform diameters. The density of polar portions of the surface (the ratio of polar to nonpolar) may differ between organic resins, and may not be uniform in a given resin.

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[36] Kielland, *J. Soc. Chem. Ind.*, 54, 232T (1935).

[37] Vanselow, *Soil Sci.*, 33, 95 (1932).

[38] Juda and Carron, *J. Am. Chem. Soc.*, 70, 3295 (1948).

[39] Davis, *Soil Sci.*, 59, 379 (1945).

[40] Boyd, Adamson, and L. S. Myers, Jr., *J. Am. Chem. Soc.*, 69, 2836 (1947).

As regards the resin phase, one factor that may be of importance in the exchange is the change in resin volume with change in *p*H of the solution, or with change in the nature or concentration of the ions present. There is also the possibility of change in particle size caused by cracking of particles under swelling and contraction changes or mechanical attrition, which might affect capacities (especially with the inorganic exchangers). Another factor might be the dissolution of organic molecules by the resin. The high densities of charge in some exchangers might certainly be expected to cause adsorbed ions and solvent to behave in a most unideal manner. The presence of occluded gases may prevent or hamper contact with the solution.

Factors outside of the resin particle may also be effective. Among these would be the changes in size of ions (hydrated radius) with change in concentration or composition of the solution. The *p*H-dependent competitions for exchange sites by solvent ions (H^+ or OH^-) may in certain cases be important.

VI. APPLICATIONS

Applications of exchangers may be classified under the headings: removal of impurities; adjustment of *p*H; analysis or separation; and preparation. In the first category fall such applications as deionization of water and water softening by exchange, the largest commercial application; purification of waste waters or recovery of valuable materials present in traces; and the removal of ionic materials from aqueous solutions of nonionic substances. In this last group would fall the removal of ionized substances from aqueous extracts of organic substances and such separations as described by Ayres,[41] in which zirconium was purified from iron and some other contaminants by converting it to the uncharged hydrous oxide which passed unchanged through the exchanger, the other cations being replaced in the solution by H^+.

In the second category above would fall those applications in which the *p*H of a solution containing exchangeable ions would be adjusted to a new value by the use of an appropriate exchanger. In this application the solution would not be contaminated by the addition of soluble acid or base; the exchanger would instead bring about a realignment of the acid–base ratio in the solution. An example of this use can be taken from Block.[42] Protein was hydrolyzed with hydrochloric acid. After removal of most of the acid by evaporation *in vacuo,* dilution with water, decolorization with charcoal, and reevaporation and dilution, the amino acid solution was still somewhat acid. The *p*H of this solution was adjusted to 6 by stirring in the free amine form of the exchange resin Amberlite IR-4, the change in *p*H upon addition of resin being followed. The resin presumably removed excess HCl and some acidic amino acids. When the desired *p*H was reached the adjusted solution could be filtered off and subjected to further procedures. The method was also used by Cannan.[43]

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[41] Ayres, *J. Am. Chem. Soc.*, 69, 2879 (1947).

[42] Block, *Proc. Soc. Exptl. Biol. Med.*, 51, 252 (1942).

Ion exchangers are proving extremely useful in analysis and separation applications in connection not only with inorganic but with organic substances.[44] Preparative applications differ from analytical separations by being carried out on a larger scale, usually without as rigorous demands on complete separations.

VII. METHODS OF USING ION EXCHANGERS

In general the batchwise use of an exchanger is not as efficient as the cascade, and this not as efficient as the differential countercurrent use (Chapter VI). There is one application, however, in which the batchwise use of the exchanger is almost obligatory, and that is in the adjustment of *p*H or any other ion concentration. Here the objective is not the removal of as much as possible of a given component with the least exchanger, but the removal up to a point. Such adjustment would be difficult with a column or bed of exchanger. The concentration would be changed past this point—would be overadjusted—at the top of the bed. Thus even though at the end of the process when all the solution was mixed the proper *p*H was reached, yet at the beginning of the process some solution would have been carried past this point because of the countercurrent arrangement. This might lead to precipitations and other undesired reactions during this period. In the batchwise operation the exchanger is introduced into the solution in portions, equilibrating the mixture after each addition, and following the change in ion concentration. The desired endpoint can be approached closely in this way without seriously overshooting it if the solution is well stirred. This type of exchanger application could probably be put to wide use, for the concentration, within reason, of almost any ion could be adjusted by the use of the appropriate exchanger. The exchangers might be used in some cases for buffering the ion concentration.

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[43] Cannan, *J. Biol. Chem.*, 152, 401 (1944).

[44] Kunin, *Anal. Chem.*, 21, 87 (1949); 22, 64 (1950).

As has been pointed out in another connection the amount of exchanger needed for a batchwise application can be calculated from the appropriate adsorption isotherm. The problem is more complicated when the exchanger is applied in a countercurrent manner for analysis or separation of several substances. The quantitative analysis of the behaviors of resins in columns has been the subject of much investigation. Much of this work has been done in connection with rare earth separations. Approaches taken have been based on the application of chromatographic theory on analogy to distillation and to heat exchange. Still another is empirical, based, so to speak, on exigency. A brief outline of some of this work (not included in Chapter VIII) is given below.

Tompkins and Mayer[45] defined an equilibrium distribution coefficient representing the concentration of an ion (a cation) in the resin phase divided by its concentration in the solution phase:

$$K_d = \frac{M_s/\text{mass of resin}}{M_l/\text{volume of solution}} = \frac{M_s}{M_l} \times \frac{\text{volume of solution}}{\text{mass of resin}}$$

Here M_s and M_l are the fractions of the ion in the solid resin and liquid phases, and K_d is the distribution coefficient at equilibrium. The solution volume was expressed in milliliters and the resin mass in grams of oven-dried resin. For the greatest precision in determining K_d, the ratio M_s/M_l should be in the range 0.5 to 2.0.

With 10 ml. of solution 0.23 M in citrate, 0.50 M in NH_4^+, and 3×10^{-4} M in Pr^{+3} or Ce^{+3} the constant K_d did not vary beyond experimental error when the amount of exchanger (Dowex-50, ammonium form) was varied from 0.686 to 12.526 g. This constancy of K_d with variation in the ratio of solution volume to mass of resin suggested that the values found could be applied to column operation if equilibrium conditions could be closely approached. A further restriction exists: the concentration of the *ion* must be sufficiently low that Henry's law is obeyed (*i.e.*, the distribution isotherm must be linear). This is achieved, in the presence of a reasonable amount of the rare earth, by complexing with citrate. The *p*H is maintained at 3.2 or below so that the complexes formed from different earths are most separable.

In the column separation of the rare earths the procedure used was elution analysis. The mixture of rare earth chlorides to be separated, containing appropriate radioactive tracers, was adsorbed at the top of the column of exchanger in a zone with a depth of the order of 2 cm. per 100 mg. of rare earth per square centimeter of bed area (Dowex-50) when the ionic strength was below 0.1.[46] The mixed zone was then developed with an appropriate citrate solution at an adjusted pH. The effluent was continuously monitored and the radioactivity plotted against effluent volume. Elution curves were thereby obtained, with each zone showing activity which rises to a maximum and then falls as the zone passes the measuring device.

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[45] Tompkins and Mayer, *J. Am. Chem. Soc.*, 69, 2859 (1947).

[46] Harris and Tompkins, *J. Am. Chem. Soc.*, 69, 2792 (1947).

The distribution coefficient K_d was utilized in an analysis of the column behavior by Mayer and Tompkins.[47] Their approach to this problem was based on analogy to fractional distillation or extraction. They considered the column of adsorbent as made up of a number of theoretical "plates," each having an equivalent mass of exchanger and volume of solution. Under conditions of flow the volume in an upper plate progresses from plate to plate down the column. A quantity C was defined to represent the distribution of the solute between the exchanger and the solution in the plate. At equilibrium, or close to it, the following relation held:

$$K_d = \frac{M_s}{M_l} \times \frac{\text{volume of solution (ml.)}}{\text{mass of resin (g.)}} = C \times \frac{\text{ml. solution}}{\text{g. resin}}$$

Since the *ratio* of solution volume to resin mass is involved, the mass of resin in the column and the volume of solution to fill this column (V) are used in the calculations.

The theoretical analysis, which will not be given here, led to the following conclusions. The ion with the lowest C value, that is, with the distribution displaced most toward the solution phase, moves most rapidly through the column. The fraction of column traversed by the zone of an ion is equal to F/C, where F is the number of V's which have passed through the column. The rate of movement of the zone down the column is Dr/C, where D is the length of the column, and r the rate of flow in V's per unit of time; and the distance between two zones is equal to DF $(1/C' - 1/C'')$, where the C's refer to the substances in the zones. The fraction of this distance over which a certain degree of overlapping of zones occurs is proportional to p^{-1}, that is, inversely proportional to the number of plates; the longer the distance traversed by the zones, then, the greater is the separation. The zones broaden as they pass through the column, the maximum concentration in the zone varying as $p^{-1/2}$. The maximum also varies as C^{-1}; thus the maxima of successive zones as several substances pass from the column represent successively smaller fractions of the initial quantities of the corresponding substances. It is evident, therefore, that the behavior predicted is quite analogous to that encountered with other distribution processes applied in a countercurrent manner.

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[47] Mayer and Tompkins, *J. Am. Chem. Soc.*, 69, 2866 (1947).

A test of the theory under near-equilibrium conditions was made with europium and element 61 under conditions where some overlapping of the zones occurred. The data are shown in Table IX-3. It is apparent that under these conditions, where finely divided resin was used and equilibrium was approached by operating at 100°, the data and theory are in good agreement.

TABLE IX-3

Comparison of Experimental Data with Theory[47] in the Region of Cross Contamination of Zones of Eu with Element 61

Volumes (V) of eluate[a]	Observed ratio of Eu to element 61	Fractional ratios of Eu to 61	
		Experimental[b]	Theoretical
6.74	100	80	110
7.23	8.18	6.7	8.0
7.47	2.45	2.0	2.14
7.57	1.50	1.22	1.3
7.67	0.762	0.62	0.74
7.73	0.423	0.34	0.48
7.98	0.164	0.133	0.135
8.18	0.064	0.052	0.050
8.36	0.024	0.020	0.021
8.57	0.006	0.005	0.007

[a] The fractions shown cover the region of cross contamination between the two zones, measured in units of V.

[b] Corrected for original ratio of Eu to element 61. C for element 61 = 9.41; C for Eu = 6.08 (see text). Cross contamination: *calculated*, 1.74 V's of solution; *found*, 1.71 for contamination just detectable by differential count, *i.e.*, 1%.

Chromatographic theory has been applied to ion exchange separations. The problem which is faced here appears to be the difficulty of approaching equilibrium conditions with a practical concentration and flow rate. The aim of a good many of the investigations has been to predict the breakthrough for deep bed or column application of the exchangers, and to predict the shape of the front of substance in the breakthrough region.[48] These experiments yield information about the capacity of the adsorbent for different ions. Related to this problem is that of predicting the elution curves for recovery of adsorbed material from the exchanger. Another problem is the prediction of the shape and rate of movement of zones. These are the same problems which have been described and discussed in Chapter VIII.

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[48] Beaton and Furnas, *Ind. Eng. Chem.*, 33, 1501 (1941); Boyd, Schubert, and Adamson, *J. Am. Chem. Soc.*, 69, 2818 (1947); Boyd, Adamson, and L. S. Myers, Jr., *ibid.*, 69, 2836 (1947); Boyd, L. S. Myers, Jr., and Adamson, *ibid.*, 69, 2849 (1947); Mayer and Tompkins, *ibid.*, 69, 2866 (1947).

In large-scale operations with ion exchangers it is often necessary to use quite concentrated solutions. Here Harned's rule that the log of the mean molal activity coefficient of an electrolyte varies linearly with concentration at constant total molality[49] is of considerable utility. It helps to simplify calculations such as those sketched above in which activities of ions are employed. Difficulties in dealing with and measuring *p*H and ion activities in systems containing suspensions of charged particles of very high valency, such as clays and ion exchangers, has been discussed by Jenny and co-workers.[50]

[49] Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926). The subject is discussed in H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 2nd ed., Reinhold, New York, 1950, P. 454 *ff*.

[50] Jenny, Nielsen, Coleman and Williams, *Science*, **112**, 164 (1950).

CHAPTER X

Partition Chromatography

I. INTRODUCTION

Partition chromatography is a method of separating substances by distributing them between two liquid phases, one of which is mobile and the other essentially fixed by sorption to a support. The support itself may or may not be active in the separation process. Partition chromatography is thus essentially a differential countercurrent application of the liquid–liquid distribution (Chapter VI). It is, however, sometimes complicated by other types of distributions. The method was developed by Martin and Synge[1] as a brilliant extension of an attempt to produce an efficient countercurrent contacting machine.[2] The background of its development has been sketched by Martin.[3] The method was originally worked out for separating mixtures of acetylated amino acids, but has been widely applied to analytical problems. A number of reviews are available.[3,4]

The subject of partition chromatography may, for convenience, be discussed under two subheads: the method using columns, the "bulk" application; and the method using strips or sheets of paper, the "one" or "two-dimensional" application. The former employs a column of silica gel, starch, etc., to which is sorbed one fluid phase, and over which the second fluid phase passes. The latter employs, for example, strips or sheets of filter paper to support the one phase, the second passing over this, driven by capillary forces. The kinds of apparatus used in these two methods are different, but the principle is the same for both. They will be discussed separately below after a brief consideration of theory.

[1] Martin and Synge, *Biochem. J.*, 35, 1358 (1941).

[2] Martin and Synge, *Biochem, J.*, 35, 91 (1941).

[3] Martin, *Ann. N. Y. Acad. Sci.*, 49, 249 (1948).

[4] Martin and Synge, *Advances in Protein Chem.*, 2, 1 (1945); Martin, "Partition Chromatography," in *Ann. Repts*, 45, 267 (1949); Martin, "Partition Chromatography," in *Biochem. Soc. Symposia*, 3, Cambridge Univ. Press, London, 1949; Clegg, *Anal. Chem.*, 22, 48 (1950); Synge, *Analyst*, 71, 256 (1946); Consden, *Nature*, 162, 359 (1948).

II. THEORY

The theory proposed by Martin and Synge[5] for the partition chromatogram was developed on analogy to that of the packed distilling column. Using the assumptions that diffusion upward and downward in the column was negligible and that the distribution constant of a solute between the two phases was not sensitive to concentration or to the presence of other solutes, they derived a relation between the parition coefficient (α) for a solute and the R value for a zone of the substance on the column. These terms are defined thus:

$$\alpha = \frac{\text{g. solute per liter of nonmobile phase}}{\text{g. solute per liter of mobile phase}}$$

$$R = \frac{\text{movement of position of maximum concentration of solute}}{\begin{array}{c}\text{simultaneous movement of surface of developing phase}\\ \text{in empty part of tube above the partition column}\end{array}}$$

The relation between these two terms is:

$$R = \frac{A}{A_L + \alpha A_S} \qquad \text{or} \qquad \alpha = \frac{A}{RA_S} - \frac{A_L}{A_S}$$

where A is the area of the cross section of the tube (or of the column), A_S that of the nonmobile phase, and A_L that of the mobile phase. That is $A_S + A_L = A -$ (area of the cross section of inert solid). The measurement of the R value for a given zone allows α to be calculated for the solute if the other quantities are known. Martin and Synge found that α determined in this way for a number of acetyl amino acids agreed well with α determined with a separatory funnel. The R value, since it is related to the distribution coefficient serves to characterize the substance. Martin and Synge set up tables of values of R for a large number of acetylated amino acids.

With paper strips and sheets the measurement of R is not at all convenient because of the nature of the apparatus. For this reason a new term R_F was defined,[6] in which the movement of the zone relative to that of the advancing front of the developer liquid (the mobile phase) is measured:

$$R_F = \frac{\text{movement of zone}}{\text{movement of advancing front of mobile phase}}$$

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[5] Martin and Synge, *Biochem. J.*, 35, 1358 (1941).

[6] Consden, Gordon, and Martin, *Biochem. J.*, 38, 224 (1944).

R_F is related to R and α as follows:

$$R_F = RA_I \qquad \frac{A_I}{A_L + \alpha A_s}$$

and

$$\alpha = \frac{A_L}{R_F A_s} \qquad \frac{A_L}{A_S} \qquad \frac{A_L}{A_S}\,\frac{-}{R_F} - 1$$

Here A is the cross-sectional area of paper + nonmobile phase + mobile phase, A_L that of the mobile and A_S that of the nonmobile phase, all in exact analogy to the partition column derivation.

The measurement of R and R_F values is relatively easy. Measurement of distance moved is made from the center of the developed zone to the center of the original zone. The distance moved by the surface of the liquid in the tube during this same period is used for determining R. To determine R_F the center of the original spot is taken as an origin and the distances to the center of the developed spot (or zone) and to the front of the developer are measured.

The concentration profile of a zone in the direction of its movement along the column or paper would be symmetrical and would take the bell shape of the normal curve of error if the distribution coefficient were constant with concentration (linear isotherm).[7] With dilute solutions this theoretical curve is approached quite well. With more concentrated solutions the concentration profile becomes unsymmetrical. If the distribution coefficient of the substance decreases with increase in concentration the more concentrated part of the zone will move faster. The front then tends to become sharper and the trailing boundary more diffuse. This behavior can be minimized by working with initially dilute solutions. It is a feature of partition chromatography that, by using dilute solutions, nearly ideal behavior may often be approached.

III. PARTITION CHROMATOGRAPHY WITH COLUMNS

This method was originated by Martin and Synge[8] for the separation of acetylated amino acids by distribution between an aqueous phase held immobilized on silica gel and a chloroform–butanol mobile phase. The method has since been applied to free amino acids, particularly by Moore and Stein,[9] who have developed and made quantitative a method based on the observation by Elsden and Synge[10] that separations of free amino acids could be made in columns in which the aqeous phase is supported on potato starch (see below). It has also been applied to the separation of fatty acids[11] and other substances.[12]

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[7] L. C. Craig and D. Craig, "Extraction and Distribution," in Weissberger, ed., *Technique of Organic Chemistry,* Vol. III, Interscience, New York, 1950, p. 171 ff.

[8] Martin and Synge, *Biochem. J.,* 35, 1358 (1941).

[9] Moore and Stein, *Ann. N. Y. Acad. Sci.,* 49, 265 (1948); Stein and Moore, *J. Biol. Chem.,* 176, 337 (1948).

1. General Description

The supporting adsorbent, equilibrated with the nonmobile phase, is charged into the chromatogram tube as a slurry and allowed to settle and pack down. Sometimes an indicator is dissolved in the nonmobile phase. When the adsorbent mixture has settled and excess mobile phase has drained off, or been sucked off, the substance to be analyzed is applied to the column by pipetting a solution of it carefully down the wall of the tube. As this solution passes into the column, developer is introduced and the development begun. The partition chromatography proceeds as any liquid chromatogram (Chapter VIII).

2. Preparation of the Adsorbent

One of the important variables in the partition chromatography seems to lie in the supporting adsorbent. Martin and Synge[13] gave the following directions for preparing a suitable silica gel support. Commercial waterglass (140° Tw.) is diluted with two volumes of water, and 10 *N* hydrochloric acid is stirred in until an acid reaction is obtained using methyl orange as an internal indicator. The gel is allowed to stand several hours, with further addition of acid, if necessary, and is then filtered and washed with distilled water on a Büchner funnel until the washings are free from indicator. The gel is allowed to age wet on the filter one or two days, is washed again, and then dried at 110°. For use with acetylated amino acids 50% (wt./wt.) of water saturated with methyl orange is added to the gel and thoroughly mixed in. A dry pink powder results.

Some variation is found between different lots of waterglass. Gordon, Martin, and Synge[14] found that with methyl orange as the indicator "good" gels have a flesh-pink background color, whereas "tailing" gels have a yellow to orange-yellow background color.

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[10] Elsden and Synge, *Biochem. J.*, 38, ix (1944); Synge, *ibid.*, 38, 285 (1944).

[11] E. L. Smith, *Biochem. J.*, 36, xxii (1942); Elsden, *ibid.*, 40, 252 (1946); Ramsey and Patterson, *J. Assoc. Offic. Agr. Chem.*, 28, 644 (1945); 29, 337 (1946); 31, 139 (1948); Cassidy and Nestler, *Discussions Faraday Soc.*, No. 7, 259 (1949).

[12] Sanger, *Biochem. J.*, 39, 507 (1945); Isherwood, *ibid.*, 40, 688 (1946); Gottlieb, *J. Am. Chem. Soc.*, 70, 423 (1948).

[13] Martin and Synge, *Biochem. J.*, 35, 1358 (1941).

[14] Gordon, Martin, and Synge, *Biochem. J.*, 38, 65 (1944).

Precipitated silica of reagent grade may serve as a supporting substance, and was used in some experiments by Martin and Synge.[13] Ramsey and Patterson[15] used a commercial silicic acid[16] in separating fatty acids. They also described the laboratory preparation of a silica gel by a method similar to that of Martin and Synge. The preparation of silica gel has also been discussed and described by Harris and Wick.[17] Peterson and Johnson[18] used Celite (Table VII-8) as a support.

Detailed directions for the preparation of starch columns suitable for the separation of free amino acids are given by Stein and Moore.[19] The starch is equilibrated with aqueous butanol containing enough water so that the final total amount of water is 30% of the dry weight of the starch. After settling and aging, the column is treated with 8-hydroxyquinoline to remove interfering metal ions.

3. Use of Indicators

Martin and his co-workers used indicators in the nonmobile phase to show up visually the presence and behavior of zones of acetylated amino acids. With methyl orange the zones appear pink.[20] Methyl orange shows the disadvantage that it is leached from the column when the alcohol content of the mobile phase is increased. Studies have been made to find more suitable indicators.[21] With free amino acids no indicator is used.[22] In separations of lower fatty acids Bromocresol Green has been found to be a satisfactory indicator,[23] though not the only suitable one.[24] The higher fatty acids, from C_{11} to C_{19}, can be separated on a partition column, but no indicator is used in this case by Ramsey and Patterson.[25]

4. Developer Solutions

Martin and Synge found,[20] and other investigators have confirmed, that the movement of zones is very sensitive to the composition of the developer solution. Thus, on silica gel columns the zones of acetylated amino acid move very slowly if the developer is pure chloroform. The addition of 1% ethanol or *n*-butanol causes the zones to move readily. Evidently the distribution of the acetylated amino acids into the mobile phase (the chloroform) is favored by the addition of the polar substance. This obviously gives latitude for the adjustment of the rate of movement of the zones. After faster zones have run from the column, the percentage of butanol can be increased so as to speed up the slower zones.[26] The composition of the developer also affects recovery. Thus, Martin and Synge[27] found that with chloroform containing 1% ethanol good separation of acetylated amino acids was obtained, but recoveries were of the order of 70%. With 1% butanol, recoveries in two experiments ranged from 81 and 79% for phenylalanine, to 93 and 98% for leucine, to 110 and 101% for the mixed valine, methionine and proline, valine, and methionine fractions. In general, then, given a suitable support, the rate of movement of the zones and their separability can be controlled. The solutes can be moved into or out of the nonmobile phase (out of or into the mobile phase) by changing the relative polarities of the phases (see Chapters III and V). For example, the distribution between water and chloroform favors the water phase for the lower acetamino acids; it can be made to favor the chloroform phase somewhat more by dissolving *n*-butanol in the chloroform. This makes the mobile phase more polar. The change in the developer speeds up the movement of the zones. As another example, Ramsey and Patterson[28] found that a mixture of furfuryl alcohol and 2-aminopyridine as the nonmobile phase and *n*-hexane as the mobile gave a satisfactory separation. Here the effect is probably quite complicated, but it is expected at least that the basic immobilized phase affects the distribution ratio by changing the ionization behavior of the acids.

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[15] Ramsey and Patterson, *J. Assoc. Offic. Agr. Chem.*, 28, 644 (1945).

[16] Mallinckrodt AR precipitated powder.

[17] Harris and Wick, *Ind. Eng. Chem., Anal. Ed.*, 18, 276 (1946).

[18] Peterson and Johnson, *J. Biol. Chem.*, 174, 775 (1948).

[19] Stein and Moore, *J. Biol. Chem.*, 176, 337 (1948).

[20] Martin and Synge, *Biochem. J.*, 35, 1358 (1941).

[21] Gordon, Martin, and Synge, *Biochem. J.*, 37, 79, 313 (1943); 38, 65 (1944); Liddell and Rydon, *ibid.*, 38, 68 (1944). Alphamine Red R is advertised by Amend Drug & Chemical Co., Inc., New York.

[22] Moore and Stein, *Ann. N. Y. Acad. Sci.*, 49, 265 (1948).

[23] Elsden, *Biochem. J.*, 40, 252 (1946); Ramsey and Patterson, *J. Assoc. Offic. Agr. Chem.*, 28, 644 (1945); 31, 139 (1948).

[24] Ramsey and Patterson, *J. Assoc. Offic. Agr. Chem.*, 28, 644 (1945).

[25] Ramsey and Patterson, *J. Assoc. Offic. Agr. Chem.*, 31, 441 (1948).

5. Qualitative Analysis

The use of *R* values permits the qualitative analysis of mixtures. The *R* value of a substance is a physical constant indirectly determined by the partition coefficient. Martin and Synge[29] report *R* values to one significant figure because of inconsistencies related to the difficulty of reproducing columns. They point out, however, that *ratios* of *R* values are much more consistent. Relative *R* values are used by Ramsey and

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[26] Martin, *Ann. N. Y. Acad. Sci.*, 49, 249 (1948).

[27] Martin and Synge, *Biochem. J.*, 35, 1358 (1941).

[28] Ramsey and Patterson, *J. Assoc. Offic. Agr. Chem.*, 31, 441 (1948).

[29] Martin, *Ann. N. Y. Acad. Sci.*, 49, 249 (1948).

[30] Ramsey and Patterson, *J. Assoc. Offic. Agr. Chem.*, 28, 644 (1945); 31, 139 (1948).

Patterson,[30] as well as threshold volume, for tentative identification of fatty acids. In carefully controlled experiments the threshold volumes varied as much as 10% for the acids C_5 to C_{10}. They observed also that the threshold volumes varied with the amount of the acid placed on the column, and this had to be taken into account, of course, in making identifications. Stein and Moore[31] found that the effluent volume at which a given amino acid peak (maximum of the zone) emerged from their starch columns was constant to within ±5%. The identity of each substance separated out on a column is usually checked by some independent means.

6. Quantitative Analysis

The quantitative analysis of mixtures separated by partition chromatography can be done by collecting the zones in suitable fractions as they emerge from the column and analyzing each. Martin and Synge[32] used an analysis of the nitrogen content of the zone to obtain the recovery percentages reported above. In an analysis of the higher monoamino acids in a wool hydrolyzate they obtained values shown in Table X-1. Ramsey and Patterson[33] found that on chromatography of the fatty acids C_5 to C_{10}, when present in admixtures, containing 2 to 20 mg. of each, with duplicate runs, recoveries were generally within ±5%, except that with 2 mg. quantities recoveries were usually somewhat high. Stein and Moore[34] report that in analyses of amino acid mixtures containing 19 components a single determination of a component present to the extent of 3% or more in the mixture was seldom in error by as much as 5%, and that the averages of several determinations gave accuracies of ±3%.

TABLE X-1

Analysis[a] of Higher Monoamino Acids in Merino 64's Wool[32]

Amino acid	Found by partition chromatography	Previous determination
Phenylalanine	1.9	1.9
Leucine, isoleucine	7.4	7.2
Proline	8.2	4.9
Valine		3.4
Methionine		0.4

[a] The figures are for nitrogen, in per cent of total nitrogen of wool.

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[31] Stein and Moore, *J. Biol. Chem.*, **176**, 337 (1948).

[32] Martin and Synge, *Biochem. J.*, **35**, 1358 (1941).

[33] Ramsey and Patterson, *J. Assoc. Offic. Agr. Chem.*, **31**, 139 (1948).

[34] Stein and Moore, *J. Biol. Chem.*, **178**, 79 (1949).

7. Examples

Two examples of the application of this method are given below. The first is the separation of the six normal fatty acids C_5 to C_{10}, inclusive.[33] The system used in this separation was isooctane as the mobile phase and methanol containing Bromocresol Green indicator as the nonmobile phase. The column was prepared by trial to contain the optimum amount of methanol. For 20 g. silicic acid this amount was more than 10 ml. of methanol and 2 to 5 ml. less than made this amount of silicic acid gummy and sticky. The proper amount of methanol, included in which was 1 ml. of indicator solution made by dissolving 200 mg. dye in 25 ml. methanol, was mixed in a mortar with 20 g. silicic acid. If the mixture was not alkaline enough to give a pale bluish-green color, 1 *N* ammonium hydroxide solution was added dropwise with thorough mixing to this point. A slurry was then produced by mixing in 60 ml. isooctane.

TABLE X-2

Data on the Separation by Partition Chromatography of a Mixture of Six Fatty Acids (Duplicate Runs)[33]

Acid	Added, mg.	Found, mg.	Recovery, %	Threshold volume, ml.
Capric	10.17	9.5	93	42
		10.1	99	43
Pelargonic	10.22	10.0	98	53
		10.1	99	53
Caprylic	10.15	10.7	105	66
		10.8	106	66
Enanthic	10.12	9.3	92	88
		9.7	96	88
Caproic	9.98	9.5	95	117
		9.6	96	119
Valeric	10.22	9.7	95	167
		9.9	97	159

This was transferred to the chromatography tube and 2 to 5 lbs. pressure applied while the tube was tapped to aid settling and packing. 10 mg. of lauric acid in isooctane was applied to the column and washed in with two 1-ml. portions of solvent followed by 15 ml. solvent. This lauric zone served to neutralize the excess ammonia on the column. The mixture containing 10 mg. of each acid was then applied to the column in 2 ml. of isooctane. Two 1-ml. portions of solvent were used to wash the last traces of mixture into the column and were applied just as the mixture itself disappeared in the column. Then the tube above the column was filled with developer and pressure applied sufficient to give a flow rate of 3 to 5 ml. per minute. The zones in the column were yellow.

The acids were collected in fractions as they passed out of the column. They appeared in the order capric, pelargonic, caprylic, etc. The data on such a run are given in Table X-2. These investigators found that in general it was possible, by one or more refractionations of the zones from a column, to detect an homologous impurity present to the extent of 0.5 to 1%.

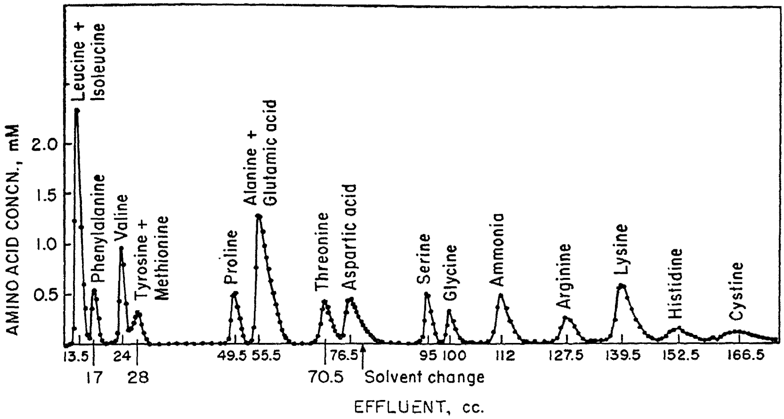

Fig. X-1. Chromatographic fractionation of a hydrolyzate of bovine serum albumin.[34] The sample corresponded to about 2.5 mg. of protein, and was separated on a 0.9 × 30 cm. column of starch. The first developer mixture was 1:2:1 1-butanol:1-propanol:0.1 *N* HCl. At the point marked, the developer was changed to 2:1 1-propanol:0.5 *N* HCl.

Stein and Moore[35] separate amino acids on a starch column. One such experiment is described in outline. The starch column was prepared in a carefully specified manner so that the total water present was 30% of the dry weight of the starch. The column was further equilibrated by running with solvent for some 36 hrs. The prepared column flowed at the rate of 2.0 to 2.4 ml. per hour per square centimeter of cross-sectional area when the column was 30 cm. high and the pressure 15 cm. of mercury. An automatic fraction collecting machine[36] was devised, and the large number of fractions which were collected were analyzed by a photometric ninhydrin method[37] worked out by these investigators. Pipetting machines and other labor-saving devices were used. By careful attention to details these authors were able to obtain effluent analysis curves such as shown in Figure X-1. This figure[38] shows the amino acid concentration, determined photometrically by reaction with ninhydrin, plotted against the effluent in cubic centimeters. The amount of amino acid is related to the area under the peaks, allowance being made for overlapping of the zones. It is reported that in analyses like these 100 ± 2% of the total protein nitrogen is accounted for. A combination of chromatograms run with three solvent systems is required for quantitative estimation of essentially all the components of acid hydrolyzates, using an amount of hydrolyzate corresponding to *ca.* 2.5 mg. of protein. Thus a complete analysis in triplicate can be carried out on some 25 to 50 mg. protein. The values for amino acids obtained by Stein and Moore from proteins agree well with published analyses by other methods.

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[35] Stein and Moore, *J. Biol. Chem.*, 176, 337 (1948); Moore and Stein, *J. Biol. Chem.*, 178, 53 (1949).

[36] Fraction collectors are advertised by American Instrument Co., New York, Microchemical Specialties Co., Shandon Scientific Co. (London), and Technicon Chromatography Corp., New York; equipment for paper partition chromatography is also made by University Apparatus Co., Berkeley, Cal.; see also Randall and Martin, *Biochem. J.*, 44, ii (1949); Cuckow, Harris, and Speed, *J. Soc. Chem. Ind.*, 68, 208 (1949).

Partition chromatography on columns suffers from the limitation that only small amounts of material can be handled conveniently. The ratio of mass of column to mass of material separated is often fairly large. Thus, for 120 mg. of fatty acid mixture 20 g. of silicic acid would be used; and for about 2.5 mg. of protein hydrolyzate, a starch column 0.9 × 30 cm. Stein and Moore[39] say that starch columns can be scaled up to 8 cm. or more in diameter, so that larger amounts of material may be handled. For such columns some device for sharpening fronts (Chapter VIII) might be needed.[40] The low capacity of the partition chromatogram column is a small price to pay for the remarkable separations which are attainable through its use.

IV. PARTITION CHROMATOGRAPHY WITH STRIPS AND SHEETS

The partition chromatography of Martin and Synge, which employs columns, was extended by Gordon, Martin, and Synge[41] to paper strips and sheets. The cellulose of the paper acts as the supporting medium, the mobile phase being an organic liquid partially miscible with water.

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[37] Moore and Stein, *J. Biol. Chem.*, **176**, 367 (1948).

[38] Stein and Moore, *J. Biol. Chem.*, **178**, 79 (1949).

[39] Stein and Moore, *J. Biol. Chem.*, **176**, 337 (1948).

[40] Claesson, *Arkiv Kemi, Mineral. Geol.*, **A23**, No. 1 (1946); Hagdahl, *Acta Chem. Scand.*, **2**, 574 (1948); Mair, *J. Research Natl. Bur. Standards*, **34**, 435 (1945).

[41] Gordon, Martin, and Synge, *Biochem. J.*, **37**, xiii (1943); Consden, Gordon, and Martin, *ibid.*, **38**, 224 (1944).

Dent[42] has suggested the name papyrography for the method. The chromatograms formed are named papergrams by Tomarelli and Florey.[43]

1. General Description

For convenience in the discussion of chromatography with paper strips and sheets the method will be described as it is used with amino acids. The principles thus illustrated are of course applicable to mixtures of other chemical types. In this method a small amount of the mixture to be separated is placed near the end of a strip of filter paper which is then arranged so that developer solvent can pass by capillarity over the mixture, carrying it along in the direction of flow of the developer. The filter paper retains an aqueous phase; the developer is an organic solvent saturated with water. The conditions are therefore present for differential countercurrent distribution (Chapter VI) as with column partition chromatography; however, with paper the solvent moves as a lamella. In practice the mixture to be separated is placed as a spot near one end of a sheet or strip of paper. This end of the paper is then dipped into the developer, which rises by capillarity into the paper. The capillary flow would cease if the paper were left exposed to the air, for eventually the rate of movement of the liquid above the solution would be balanced by the evaporation from the large surface of the film. Therefore, the strip, or sheet, is confined in a chamber which is sealed. Under these conditions the solvent front may move a considerable distance along the paper. In practice, with full-sized strips or sheets, the solvent front may travel 30 to 50 cm. beyond the point of original application of the mixture which is usually itself about 1 to 3 cm. away from the top of the developer liquid into which the paper dips.

After the solvent front has moved sufficiently far, the chamber is opened, the strip or sheet removed, and examined for separated spots as described below. The various substances are separated on the basis of their distribution coefficients. Those tending most to the organic phase move faster than the others. When a filter paper strip is used the method is called one-dimensional chromatography, referring to the single direction of development. (Since the solvent moves as a lamella it is really a "two-dimensional" *system.*) The spot of mixture may be placed at one corner of a sheet of paper and run in a given solvent. Then the sheet may be removed from the chamber and dried. The spots have been developed in this run vertically along one side of the paper. The dried paper is turned through a right angle and the row of spots is developed with a new solvent. In this second run each spot is developed in a direction at a right angle to that of its original movement. There is thus obtained a "two-dimensional" chromatogram, a diagram of spots the pattern of which, after some experience, allows individual known substances to be recognized. This is a double application of the strip method. (See Figure X-6.)

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[42] Dent, *Biochem. J.*, **43**, 169 (1948).

[43] Tomarelli and Florey, *Science*, **107**, 630 (1948). Other names suggested are *eography*, by Strain (*Anal. Chem.*, *22*, 41 (1950)), and *partography*, by Rockland and Dunn (*Science*, **111**, 332 (1950)).

It is obvious that the apparatus used with paper strips and sheets must be different from that used for column chromatography. The solvent can be run upward or downward, but the paper must be kept in an atmosphere saturated with the solvents used.

2. Apparatus

In Figure X-2 is shown an apparatus devised by Consden, Gordon, and Martin[44] for use with paper strips and downward flow of solvent.

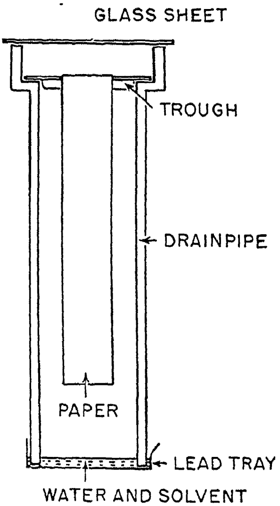

Fig. X-2. Apparatus for paper strip chromatography, according to Consden, Gordon, and Martin.[44] The paper strip hangs in a controlled atmosphere. The upper edge of the paper dips into the trough of developer liquid. (See Figure X-3.)

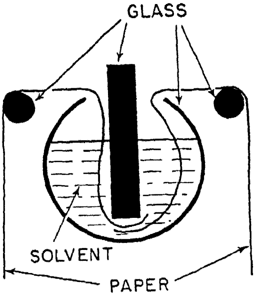

Fig. X-3. Cross section of a trough in use.[44] One end of the paper strip or sheet dips into the developer solvent and is held down by a plate. Glass spacer rods hold the paper away from the edges of the trough to prevent siphoning of the liquid.

In this apparatus the container is a drain pipe, but a glass cylinder may be used, the trough being supported, in this case, on long glass legs. The glass cylinder is better in some respects because it can be cleaned and used with different solvents at different times, whereas the pipe is somewhat porous, in spite of the glaze, and so must be kept for use with only one solvent. Figure X-3 shows a cross section of a trough with the paper dipping into the developer solvent and weighted down with a glass plate. The paper is held away from the edges of the trough by glass supporting rods. This prevents siphoning. The spots of mixture are placed so that they lie just below the rod. Many modifications of this apparatus have been suggested.[45] When sheets of filter paper are used in this method the troughs need to be fairly long, and the apparatus must be enclosed in a box. Glass-lined steel troughs[46] 34 in. long are commercially available from The Pfaudler Company, Rochester, New York. Longenecker[47] has described how to make glass troughs.

Exceedingly simple apparatus may be used by running the chromatography by capillary ascent instead of by the original capillary descending method. Capillary ascent in this application was reported by Horne and Pollard[48] and Williams and Kirby.[49] The filter paper is formed into a cylinder by bringing two opposite edges together and stapling them without their quite touching, or the edges may be doubled back and stapled first to give stiffness (Fig. X-4). The cylinder so formed is stood in developer solvent at the bottom of a glass jar or in a dish at the bottom of a glass jar or cylinder. Depending on the size of the paper, one can use 1-liter cylinders or museum or similar jars. With large jars several concentrically placed paper cylinders can be used, but they must not touch. The jars must be closed and sealed as with the descending method. The developer liquid moves up the paper in this method, otherwise the chromatogram is developed in the usual way. In these methods the spot of substance to be analyzed is placed at such a

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[44] Consden, Gordon, and Martin, *Biochem. J.*, 38, 224 (1944).

[45] Steward, Stepka, and Thompson, *Science*, 107, 451 (1948); Williams and Kirby, *ibid.*, 107, 481 (1948); Winsten, *ibid.*, 107, 605 (1948); Urbach, *ibid.*, 109, 259 (1949); Wender and Gage, *ibid.*, 109, 287 (1949); Rockland and Dunn, *ibid.*, 109, 539 (1949); Wolfson, Cohn, and Devaney, *ibid.*, 109, 541 (1949); Ma and Fontaine, *ibid.*, 110, 232 (1949); Mitchell and Haskins, *ibid.*, 110, 278 (1949); Haugaard and Kroner, *J. Am. Chem. Soc.*, 70, 2135 (1948); Yanofsky, Wasserman, and Bonner, *Science*, 111, 61 (1950); Longenecker, *Anal. Chem.*, 21, 1402 (1949).

[46] Steward, Stepka, and Thompson, *Science*, 107, 451 (1948).

[47] Longenecker, *Science*, 107, 23 (1948).

[48] Horne and Pollard, *J. Bact.*, 55, 231 (1948).

[49] Williams and Kirby, *Science*, 107, 481 (1948).

distance in from the edge of the strip as to be well above the surface of the bulk developer into which the paper dips. It should be just beyond the edge of the supporting rod in downward development, and about 2 cm. above the liquid in ordinary upward development. Rockland and Dunn[51] have modified the method by the use of paper strips in test tubes (Fig. X-5). Urbach[52] has published a method of depositing materials on paper strips with simultaneous concentration of the deposited material, so that small, concentrated spots may be obtained from dilute solutions.[53]

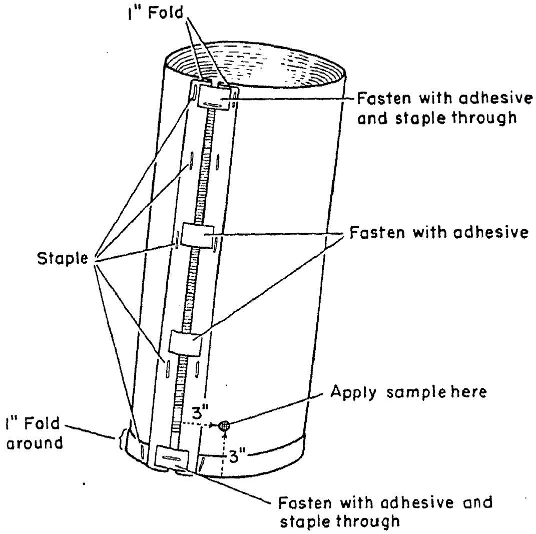
1" Fold
Fasten with adhesive and staple through
Fasten with adhesive
Staple
Apply sample here
3"
3"
1" Fold around
Fasten with adhesive and staple through

Fig. X-4. The figure shows the method of folding and fastening large sheets of filter paper for upward-flow chromatography.[50] The sample may be applied in the lower left-hand corner of the sheet, as shown here, or in the lower right, as shown in Dent's "map" in the Figure X-6. The use of adhesive tape is seldom necessary.

3. Developers

The separations obtained in partition chromatography of amino acids on paper depend a great deal on the nature of the developer. Although such liquids as benzyl alcohol, *o*-, *m*-, and *p*-cresols, isobutyric acid, *tert*-amyl alcohol, and many others have been tested, the best all-around solvents are phenol, "collidine," and *n*-butanol, introduced by Consden, Gordon, and Martin[54] to serve as acidic, basic, and neutral developers.

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[50] Wolfson, Cohn, and Devaney, *Science*, 109, 541 (1949).
[51] Rockland and Dunn, *Science*, 109, 539 (1949).
[52] Urbach, *Science*, 109, 259 (1949).
[53] Yanofsky, Wasserman, and Bonner, *Science*, 111, 61 (1950).

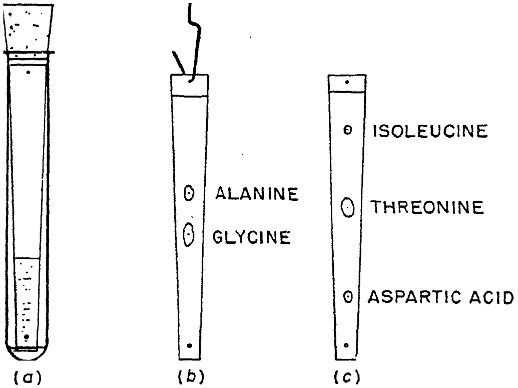

Fig. X-5. Micro method of paper strip chromatography.[51] The sample is placed at the spot near the lower edge of the strip, which is then dipped into the developer in the test tube. The wide part of the paper at the top keeps the strip vertical. Beginning development is shown in (*a*), and two chromatograms in (*b*) and (*c*).

To produce the developer the appropriate organic solvent is saturated with water or brought to some definite water content. One developer is used to spread apart amino acids which with another developer may run along together. For example, the movement of the basic amino acids is slowed by acidic conditions which are yet not sufficiently acidic to affect the neutral amino acids. Dent[55] uses this as a test of basicity; during a phenol run a beaker of 50% (v/v) acetic acid is introduced into the chamber, whereupon the basic amino acids run more slowly. The effect is more marked the more basic is the amino acid. Since acidity affects the movement of the zones, it is necessary to neutralize excess acidity in the mixture applied to the paper. If the mixture is from a protein hydrolyzate, as much HCl as possible is removed by repeated evaporation *in vacuo*, and then the spot is applied while the paper is held over a small beaker of ammonia water.

[54] Consden, Gordon, and Martin, *Biochem. J.*, 38, 224 (1944).

[55] Dent, *Biochem. J.*, 43, 169 (1948).

Dent[55] observed that pure *sym*-collidine (2,4,6-trimethylpyridine) does not give as good development as a mixture of 1 volume 2,4-lutidine and 1 volume 2,4,6-collidine, which is then saturated with water. If the pure substances are not available the fraction of pyridine bases boiling around 160° may serve. The rate of movement of the spots with this mixture can be slowed by mixing in some of the 170° fraction. Dent has observed that if 5 ml. of "good" collidine is mixed with 5 ml. water and equilibrated at about 23° only about 1 ml. water remains undissolved; if the amount of water measured more than 1.5 ml. the collidine gave uselessly low R_F values.

Discolorations are sometimes observed when ordinary phenol is used in paper chromatography, particularly in an atmosphere containing ammonia. The brownish or black material formed runs fast. It seems to be produced by catalytic action of heavy metals in the paper.[56] The discoloration is prevented by the use of cupron in the developer (0.1%) or by adding a little KCN or NaCN (*ca.* 0.1 g.) to the phenol in the bottom of the jar or cabinet. This produces a little HCN in the atmosphere about the paper. Draper and Pollard[57] purify their phenol by liquefying the crystals with 12% water, adding 0.1% aluminum turnings and 0.05% $NaHCO_3$ and distilling. After the azeotrope was distilled at atmospheric pressure the phenol was taken off at water-pump vacuum with an air condenser. Merck reagent phenol does not give this trouble. Rockland and Dunn[58] find the discoloration a convenient marker for the solvent front in their micro method. According to Draper and Pollard[57] the optimum water content for phenol is between 24 and 28%, preferably 25%. This could be tested by mixing 500 mg. NaCl with 10 ml. phenol–water solution. After thorough shaking and standing for about 20 min. the phase boundary should be at 1.4 ml. when the water content is 25%. The phenol should not be saturated, they say, since the presence of a water layer in the chromatography chamber leads to incorrect results. Erratic R_F values were observed with saturated phenol by Bull, Hahn, and Baptist,[59] who recommend 80% phenol. They give a table showing the variation of a number of R_F values as a function of phenol concentration. The amino acids most sensitive to changes in phenol concentration are aspartic, glutamic, lysine, and arginine.

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[56] Consden, Gordon, and Martin, *Biochem. J.*, 38, 224 (1944).

[57] Draper and Pollard, *Science,* 109, 448 (1949).

[58] Rockland and Dunn, *Science,* 109, 539 (1949).

[59] Bull, Hahn, and Baptist, *J. Am. Chem. Soc.*, 71, 550 (1949).

4. Procedure for Strips

The filter paper,[60] which may be cut 1.5 cm. wide or more, is cut from sheets. The developer may run at a rate which is different *with* the machine direction of the paper from the rate *across* the machine direction; thus for comparable results the strips should be cut in the same direction. The machine direction can be determined by dipping into distilled water short strips cut parallel to and at right angles to one edge of the paper sheet. The strip in which the water rises more rapidly is cut with the machine direction of the paper. If a drop of water is placed on the paper it spreads to an oval, the longer axis of which is in the machine direction of the paper. The strip is marked lightly with a pencil line, the line of origin, at an appropriate distance from one end. The distance from the end depends upon the apparatus, see above. About 2 to 4 μl. (microliter) of solution containing 5 to 15 μg. of each amino acid to be tested is deposited at a marked point on this line and let dry. Depending on the width of the paper several spots may be placed along the line. The distance apart depends on the volume of liquid applied, but the spots should not be closer to each other than 1 cm. They should not be placed too near the vertical edge of the paper. Standard solutions if made in 75% (v/v) ethanol are stable for months.[61] Such solutions should be about 0.01 M with the amino acid, and 5 to 10 μl. is used for a spot. A little HCl can be used with this solvent to bring less soluble amino acids into solution. To obtain mixtures a spot of one amino acid can be placed on top of another provided the first spot is allowed to dry before the second is applied. In order to get more material onto the paper the amino acid mixture can be streaked along the origin line, thus forming a wide zone.[62]

For downward development the upper edge of the paper is placed in the trough (Fig. X-3) and held down with a glass bar, or a rod bent at one end to give a handle. For upward development the strip, which must be sufficiently wide, is curved into a cylinder and the edges stapled together so that they just do not touch (Fig. X-4). In this case the line of spots forms a circle around the outside of the paper cylinder near the lower end. This end is carefully lowered into the developer in the bottom of the chamber, so that the line of wetting is even, and the cylinder stands vertical.

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[60] Whatman No. 1 or 3; or Carl Schleicher and Schuell No. 507 or 595. Other papers are better in special applications—see Kowkabany and Cassidy, *Anal. Chem.*, 22, 817 (1950).

[61] Dent, *Biochem. J.*, 43, 169 (1948).

[62] Yanofsky, Wasserman, and Bonner, *Science*, 111, 61 (1950).

The solvent front moves faster at first then slows down. After 18 to 36 hrs. it has traversed the distance from the line of spots to within a few centimeters of the far edge of the strip or sheet (30 to 50 cm.). The paper is then removed from the chamber, the position of the solvent front marked lightly in pencil, and the paper dried. It is then sprayed lightly with a solution of ninhydrin (0.1% solution in *n*-butanol) and allowed to dry. The paper is then heated 5 min. at about 80° to develop the ninhydrin color, and the zones so produced are outlined in pencil with a dot at the center of gravity of the color. Dent[63] recommends letting the ninhydrin reaction proceed at room temperature for about 24 hrs., as this avoids the danger of fading of the spots due to overheating; however, in other experiences exposure to light is much more conducive to fading than exposure to heat. For quantitative analyses more precautions must be taken. The sensitivity of the ninhydrin reaction has been investigated by Pratt and Auclair.[64] These investigators suggest viewing the chromatogram by transmitted light.

5. Procedure for Sheets

The procedure is the same as above with the following exceptions. One spot is placed near one corner of a sheet at a spot marked lightly with a pencil (Fig. X-4). The chromatogram is developed. If phenol and collidine are to be used the phenol may be used first,[63] or the collidine. After the first development the sheet is dried, turned through a right angle, and developed with the second solvent. Following this development the sheet is dried, sprayed with ninhydrin, and the color reaction is brought out.

6. Rate of Movement of Zones

The R_F values can be obtained from the chromatogram by measuring the distance moved by the center of gravity of the zone from the origin mark and dividing this by the distance moved by the developer front from this point. An elastic device for this has been described by Phillips.[65] R_F values are, however, so sensitive to many extraneous variables that individual values are not very reliable. Ratios of the values are more reliable, as many of the variables may be canceled. Usually some known amino acids are added to the mixture or run with it on the same strip to calibrate the chromatogram. Dent says that the most reliable identification in the two-dimensional chromatogram comes from the pattern of the spots which is remarkably constant.

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[63] Dent, *Biochem. J.*, 43, 169 (1948).

[64] Pratt, Jr., and Auclair, *Science*, 108, 213 (1948).

[65] Phillips, *Nature*, 162, 29 (1948). Rockland and Dunn (*Science*, 111, 332 (1950)) have devised a *partogrid*, a geometric proportional divider for determining R_F values.

7. Qualitative Analysis

The relative R_F values and the pattern of the spots serve for identification of known amino acids and other compounds which give the ninhydrin color. For more positive identification several tests have been suggested. Sulfur-containing amino acids can be identified by comparing a normal two-dimensional chromatogram with one obtained after the solution has been treated with H_2O_2. The oxidized amino acids give a different pattern (see, for example, methionine and methionine sulfone and sulfoxide, Figure X-6). The oxidation is carried out with hydrogen peroxide applied to the spot on the paper, or mixed with the sample.[66] A trace of ammonium molybdate (10 to 20 μl. of 0.02% solution) on the spot on the paper helps the peroxide to convert methionine and its sulfoxide to the sulfone.[67] Winegard, Toennies, and Block[68] use a reaction with potassium iodoplatinate, and Chargaff, Levine, and Greene[69] use the ability of sulfur-containing amino acids to catalyze the oxidation of sodium azide by iodine as a means of recognizing these substances on the filter paper. Patton and Foreman[70] reported that by spraying the paper with *o*-phthalaldehyde, glycine can be recognized as a green spot, ammonium as dark gray, and histidine and tryptophane as separate, intense yellow-fluorescing (under radiation of *ca.* 3650 A.) spots. They used as developer 77% ethanol because aromatic solvent mixtures gave abnormal reactions with the test reagent. Other specific tests can be used, as well as the characteristic colors given by ninhydrin itself, such as yellow with the prolines. A very thorough discussion of the subject has been given by Dent.[67]

Amino acids (and other substances) can be characterized by adding to the mixture a known sample of the suspected substance. If it falls on the other, as shown by increased size of the spot, the identification is made more certain. It becomes still more certain if the known sample can be obtained in a radioactive form. If the two amino acids are the same then the position by ninhydrin development of the mixed spot will coincide with that of the radioactive spot, as determined by a radioautograph, and the detailed image, including all the irregularities in shape which occur

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[66] Dent, *Biochem. J.*, 41, 240 (1947).

[67] Dent, *Biochem. J.*, 43, 169 (1948).

[68] Winegard, Toennies, and Block, *Science*, 108, 506 (1948).

[69] Chargaff, Levine, and Green, *J. Biol. Chem.*, 175, 67 (1948).

[70] Patton and Foreman, *Science*, 109, 339 (1949).

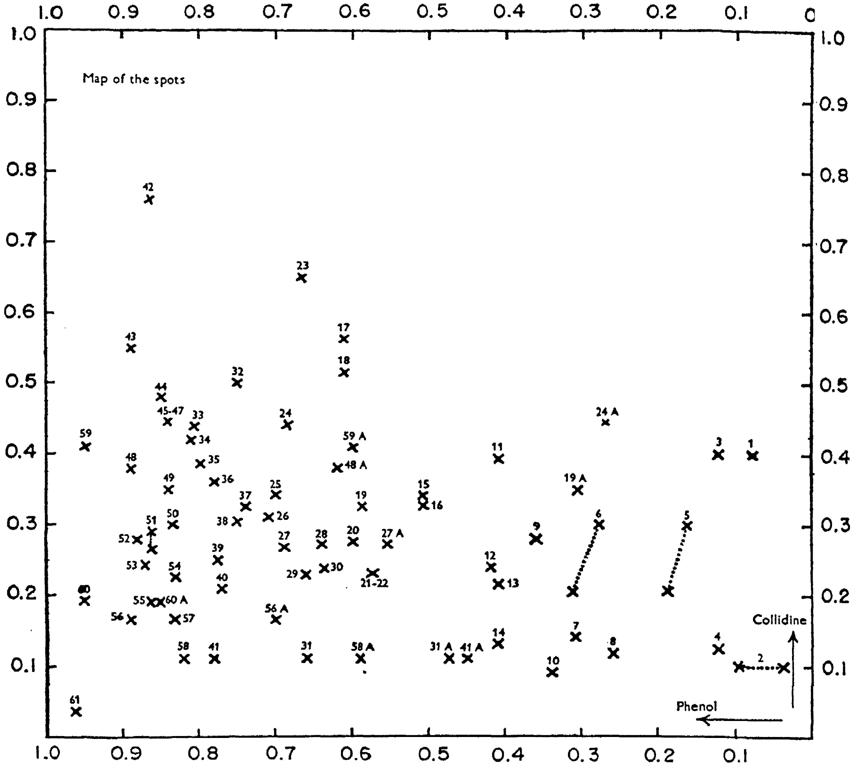

Fig. X-6. Map of spots of substances which react with ninhydrin, showing the average positions taken on phenol–collidine two-dimensional development.[74] Dent discusses the color(s) given by these substances and the behaviors of the spots, and other characteristics of the substances. α-Alanine (20); β-alanine (29); allothreonine (15)*; α-amino-*n*-butyric acid (26); α-aminoisobutyric acid (37)*; γ-aminobutyric acid (40); ε-aminohexanoic acid (55)*; α-amino-ε-hydroxycaproic acid (38)*; α-amino-octanoic acid (43)*; δ-aminopentanoic acid (57)*; α-aminophenylacetic acid (33)*; arginine (56); asparagine (13); aspartic acid (5); carnosine (54); citrulline (30); cystathionine (7); cysteic acid (1); cysteine and cystine, not usually seen; diiodotyrosine (17); β,β′-dimethylcysteine,* usually decomposes; djenkolic acid (14)*; ethanolamine (48); ethanolamine–phosphoric acid (10); glucosamine (24); glutamic acid (6); glutamine (21); glutathione (4)*; glycine (12); histamine (59); histidine (27); homocysteic acid (3)*; homocystine, does not appear because of decomposition; hydroxylysine (31); hydroxyproline (28); lanthionine (8)*; leucine (45); isoleucine (46); lysine (58); methionine (34); methionine sulfone (25); methionine sulfoxide (39); α-methyl-α amino-*n*-butyric acid (49)*; methylhistidine (51); monoiodotyrosine (23)*; norleucine, (47); norvaline (35); ornithine (41); penicillamine, see β,β′-dimethylcysteine, above; phenylalanine (44); proline (52); serine (9); serine–phosphoric acid (2); taurine (11); β,β,β′,β′-tetramethylcystine (oxidized penicillamine) (19)*; threonine (16); thyroxine (42); tryptophane (32); tyrosine (18); "under-alanine" (22); valine (36). The following substances are unknowns: fast-aminobutyric acid" (50); "fast-arginine" (60); "green-spot" (53); "nephrosis-peptide" (61). The values marked with an asterisk (*) are for substances which have been run only a few times, and Dent suggests that they be accepted with more reserve than those for the other substances.

in these spots, will be exactly the same for the ninhydrin spot and the radioautograph.[71] The amino acid in a zone may be extracted from the paper and examined by electron diffraction methods, which in some cases gives good results, or by x-rays. With 50 μg. of material Christ, Burton, and Botty[72] were able to obtain satisfactory, reproducible diffraction patterns from known amino acids by means of which unknowns could be identified.

Consden, Gordon, and Martin[73] point out that the chemical nature of the amino acids influence greatly their position on the chromatogram. In two-dimensional chromatograms, with most of the solvents, glycine, alanine, norvaline, and norleucine fall on a smooth curve which sets the pattern for the identification of the other acids. Branching of the chain results in a slight deviation from this curve and a slowing of the rate. The presence of OH decreases the R_F value in phenol, but has little effect in collidine, so with this pair of solvents serine, threonine, tyrosine, and hydroxyproline appear almost on a line (in the phenol direction) with the corresponding unsubstituted amino acids. Thus, from an examination of a two-dimensional chromatogram one can often hazard a good guess about the nature of an unknown in a new spot. Dent[74] has given a comprehensive map of the spots of ninhydrin-reacting substances. (See Fig. X-6.)

8. Quantitative Analysis

In paper chromatography it is possible to get some rough idea of the amount of amino acid present from the size and intensity of the spots relative to others.[75] Attempts have been made to make the method quantitative. These attempts are of several types. One procedure is to develop the color in a reproducible manner and then determine the percentage of light transmission along the strip and through the spot.[76] From this measurement, with suitable precautions and calibrations, an estimate of the amount of amino acids can be obtained. Bull, Hahn, and

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[71] R. M. Fink, Dent, and K. Fink, *Nature,* 160, 801 (1947).

[72] Christ, Burton, and Botty, *Science,* 108, 91 (1948).

[73] Consden, Gordon, and Martin, *Biochem. J.,* 38, 224 (1944). See also Martin, *Ann. Repts.,* 45, 267 (1949); *Biochemical Society Symposia,* 3, Cambridge Univ. Press, London (1949).

[74] Dent, *Biochem. J.,* 43, 169 (1948).

[75] Fisher, Parsons, and Morrison, *Nature,* 161, 764 (1948).

[76] Bull, Hahn, and Baptist, *J. Am. Chem. Soc.,* 71, 550 (1949); Rockland and Dunn, *ibid.,* 71, 4121 (1949); Block, *Science,* 108, 608 (1948); Fosdick and Blackwell, *Science,* 109, 314 (1949); Müller and Clegg, *Anal. Chem.,* 21, 1123 (1949).

Baptist have discussed the variables present. Another method uses radioisotope dilution,[77] or copper complexes.[78]

9. Some Variables Encountered

Consden, Gordon, and Martin[79] have discussed some of the variables which influence the results with this method. Changes in temperature of more than about 5° during a run seem to be harmful; sometimes the paper becomes waterlogged and the front disappears. Rise in temperature speeds up movement of zones with phenol–water; with collidine, fall in temperature speeds up zones.[79] Inorganic salts, if present to a high amount, cause difficulty by taking up water from the atmosphere and causing local water-logging of the paper, with distortion of the zones. The effect may be eliminated by equilibrating the solvents with saturated salt solution and impregnating the paper with salt, but then the ninhydrin colors are fainter and the flow rates slower. Some ingredients of even the purest paper may cause pink "beards" to appear, running just ahead of some spots. This is thought to be because of copper in the paper.[79] It can be eliminated by the use of agents which form heavy metal complexes, such as HCN, H_2S, in the atmosphere of the chamber, or cupron (fresh 0.1% solution) in the developer solution. Different papers have very different properties,[80] some giving inversions of spots or differently colored spots with ninhydrin. The quantity of amino acid has little effect on the R_F value, but if spots are too large they will have to move further to be separated. By using very small spots Rockland and Dunn[81] obtained separations within two to three hours. They used about 0.03 M solutions of amino acids and spots 1.5 mm. in diameter made with 0.0002 ml. of solution (see Fig. X-5). Small spots do not have to move as far to become separated. It has been observed that the farther the distance between trough and starting point of the amino acid spot the smaller the R_F value. but this variable is not serious for usual working distances.[79] It seems that optically active amino acids and racemic mixtures travel similarly on the paper.[80] Dent[80] reports that some batches of "ninhydrin" which he has obtained have failed entirely to give color reactions with amino acids.

Examples of the use of these methods, with further technical details and a description of the determination of the structure of a polypeptide (gramicidin-S) can be found in the papers of Consden, Gordon, Martin, and Synge.[82] The method is appropriate for analysis and control. The limitation of the amount of material which can be handled by the paper may be overcome somewhat by using heavy sheets of pulp, or many sheets tightly wrapped together.[83] All of these chromatographic methods are in rapid development.[84]

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[77] Woiwood, *Nature*, **161**, 169 (1948); Naftalin, *ibid.*, **161**, 763 (1948).

[78] Referred to by Martin, *Ann. Repts.*, **45**, 280 (1949).

[79] Consden, Gordon, and Martin, *Biochem. J.*, **38**, 224 (1944).

[80] Dent, *Biochem. J.*, **43**, 169 (1948); see also Kowkabany and Cassidy, *Anal. Chem.*, **22**, 817 (1950).

[81] Rockland and Dunn, *Science*, **109**, 539 (1949).

V. SOME FURTHER CONSIDERATIONS

There have been worked out many types of partition chromatography which are similar to those of chromatography described in Chapter VIII. Thus the conventional *development analysis* finds its counterpart in the conventional partition chromatography, described above, in which the separate zones are obtained from an initial mixed zone by the use of a developer solvent. If the zones are washed through the chromatographic column, or off the edge of the paper strip or sheet, the process is *elution analysis*: the liquid chromatogram.[85] A method similar to *frontal analysis* may be used (the capillary analysis of Schoenbein and Goppelsroeder[86] is of this type), and *displacement analysis,* analogous to that described in Chapter VIII has been suggested for partition chromatography.[87] That these analogies do not rest on chance is suggested by the theme developed in Chapter VI. Indeed, in the chromatographic field it is often a moot question whether a separation is due to adsorption distribution or to liquid-liquid distribution, or to a combination of the two. Thus separations are obtained on paper chromatograms using pure solvents such as water. Martin[88] has suggested that in such cases the nonmobile phase may be considered as a strong "solution" of polysaccharide in water. Other examples of this kind have been reported with paper strips and sheets and with columns.[89] It may not be out of place to suggest that because starch columns or paper strips are used in a separation process one is not *necessarily* dealing with partition chromatography.

The elegant amino acid separation method developed by Moore and Stein, using carefully prepared starch columns (see above) has been very widely used in spite of its rather tedious nature because it has given quantitative results with small quantities of hydrolyzate. It has, indeed, been the best method available for separating amino acids, being more satisfactory than previous methods using charcoal, or clays and other exchangers.[90] These authors[91] have reported an improved method using an ion exchanger which may turn out to be superior even to the starch column method.

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[82] Gordon, Martin, and Synge, *Biochem. J.*, 37, 86 (1943); Consden, Gordon, and Martin, *ibid.*, 41, 590 (1947); Consden, Gordon, Martin, and Synge, *ibid.*, 41, 596 (1947).

[83] Tatum and Adelberg, *private communication.*

[84] Martin, *Ann. Repts.*, 45, 267 (1949); *Biochem. Soc. Symposia,* 3, Cambridge Univ. Press, London, 1949; Clegg, *Anal. Chem.*, 22, 48 (1950).

[85] Partridge, *Biochem. J.*, 44, 521 (1949); *Nature*, 164, 443 (1949).

[86] F. Goppelsroeder, *Capillaranalyse*, Birkhäuser, Basel, 1901.

[87] Martin, *Biochem. Soc. Symposia*, 3, Cambridge Univ. Press. London, 1949, p. 4.

[88] Martin, *Ann. Rev. Biochem.*, 19, 517 (1950).

[89] Moore and Stein, *Ann. N. Y. Acad. Sci.*, 49, 265 (1948).

When working with the minute amounts of material which can be handled by partition chromatography, disturbing phenomena appear which might not otherwise be noticed; trace impurities, for example, may become important. Martin and co-workers have called attention to the effects of metal ions in paper[92] and have given directions for dealing with this problem. Filter paper is made in many grades, and these may differ widely in their behavior.[93] Even the best filter paper may contain soluble material. Paper may contain three forms of cellulose, classified on the basis of their solubility behaviors[94]: α-cellulose is insoluble in strong sodium hydroxide solution; β and γ forms are soluble, but the β is precipitated by mineral acid from the alkaline solution, while the γ remains soluble. The β and γ forms are thought to be degraded cellulose, possibly also oxidized. A good filter paper should contain about 95% or more of α-cellulose,[95] and reducing substances (as determined by a copper number[96]) should be present in very small amount. Some acid washed papers have been observed to yield considerable soluble material. Pure cellulose seems to be slightly soluble in water.[97] It is evident that, as Scribner and Wilson say,[98] "filter paper cannot be considered as an inert material even toward water."

Native cellulose contains firmly bound water, estimated at 5.9% by Martin.[88] When swollen with water, cellulose may take up 30% of its weight in water. When filter paper is dipped into water the water rises in the paper at a rate which decreases with time. Ostwald[99] found that the relation:

$$s = Kt^m$$

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[90] For a review, see Martin and Synge, *Advances in Protein Chem.*, 2, 1 (1945).

[91] Stein and Moore, *Cold Spring Harbor Symposia Quant. Biol.*, 14, 179 (1949).

[92] Consden, Gordon, and Martin, *Biochem. J.*, 38, 224 (1944).

[93] Kowkabany and Cassidy, *Anal. Chem.*, 22, 817 (1950).

[94] Scribner and Wilson, *J. Research Natl. Bur. Standards*, 34, 453 (1945).

[95] *Testing Methods, Recommended Practices, and Specifications of the Tech. Assoc. of the Pulp and Paper Ind.*, 1947, T 429 m-44; T 471 sm-46.

[96] *TAPPI* T 430 m-47.

[97] Strachan, *Nature*, 141, 332 (1938).

[98] Scribner and Wilson, *J. Research Natl. Bur. Standards*, 39, 21 (1947).

[99] Wo. Ostwald, *Kolloid-Z.*, 2, suppl. II, xx (1908).

describes the height risen (s) in the time t. K and m are constants which are different with different liquids. This phenomenon was further studied by Lucas.[100] When distilled water is filtered through filter paper the rate of flow (in continuous filtration) usually slows with time, often markedly. Thus at the end of two hours the rate might decrease to 2.5% of the initial rate.[101] An examination of the causes of this behavior[102] indicated that it was not explained by swelling of the fibers, for similar phenomena were observed when oil, which does not swell the fibers, was used,[103] and when the filter was of porcelain, glass, or quartz.[104]. The phenomenon was not explained by air in the filter, or by clogging of the pores by particles of mold, etc., which might possibly be present in the water. Drying out the paper substantially restored the original speed. The most consistent improvement in constancy of rate of filtration was obtained by prefiltering the water or other solution being used. Slowed filters could be speeded up by various means which suggested that the effect of slowing was produced by polarization caused by the flow of liquid through the paper. The subject may have implications in partition chromatography. Rutter[105] has suggested that the streaming potential generated in a chromatographic process may affect the movement of some constituents. This has been discussed briefly by Martin.[106]

Preliminary examination of some of the factors which control the rate of rise of liquid in paper, and separability of amino acids,[107] has confirmed that the rate of rise is inversely correlated with the viscosity of a mixture of given components,[99] but is not related to refractive index, or surface tension of the mixture. With fast rise, spots of amino acid tend to become somewhat diffuse. The R_F value decreases the further along the strip or sheet that the initial spot is placed from the solvent line.[108] The variation is linear with the distance, and the effect (tested in the collidine-water system) is the same whether the paper strip used is taken from washed, or "brown front" regions.[107] The paper appears to sorb[109] water preferentially from organic liquid mixtures, so that at the advancing front of the solvent there is a very marked concentration gradient. This seems to occur even with "equilibrated" papers. The equilibration process is very slow. For example, paper hung in a collidine-water atmosphere at room temperature was still gaining weight after 46 hours, at which time the weight which had been gained was 16.5–17% of the dry weight.[107]

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[100] Lucas, *Kolloid-Z.*, 21, 105, 192 (1917).

[101] Griffin and Parish, *Ind. Eng. Chem.*, 14, 199 (1922).

[102] Bogaty and Carson, *J. Research Natl. Bur. Standards*, 33, 353 (1944).

[103] Lane, referred to by Bogaty and Carson, *ibid.*

[104] Simon and Neth, *Z. anorg. allgem. Chem.*, 168, 221 (1927).

[105] Rutter, *Nature*, 163, 487 (1949).

[106] Martin, *Ann. Rev. Biochem.*, 19, 517 (1950).

[107] Kowkabany, *Dissertation.* Yale University.

[108] Consden, Gordon, and Martin, *Biochem. J.*, 38, 224 (1944).

[109] *Sorption* is a term introduced by McBain (J. W. McBain, *The Sorption of Gases by Solids*, Routledge, London, 1932) to cover processes in which either adsorption or absorption, or both, may be involved.

A number of variables encountered with this method were stated in the previous section. Several further points may be mentioned. In working with radioactive tracers, where zones on paper are recognized by exposing an x-ray film to the paper[110] (the radioautographic method), it should be remembered that many chemical substances can "expose" a film. For a spot on such a film to be attributable to radioactive tracer, one has to rule out the possibility of chemical development. A subtle type of difficulty was observed by Stepka and Goodwin.[111] A glycoside containing several sugar residues was examined in a two-dimensional chromatogram. It moved as a single spot in phenol. In the second development the butanol-acetic acid solvent used cleaved off glucose, which then appeared in an atypical position.

Many years ago, Langmuir[112] showed how the Traube rule implied that in any homologous series the addition of a CH_2 group in the molecule increased the energy of transfer of the molecule from a bulk to an interfacial phase by a regular amount (see Chapter I). This concept was later brought by Langmuir[113] into a more generalized theory with which he attempted to interpret the distribution and orientation of molecules in solution, between vapor and liquid, liquid and liquid, and liquid and surface phases. In the development of this theory Langmuir pointed out that the physical properties of relatively nonpolar organic molecules are usually roughly additive. Thus the addition of each CH_2 group to a chain in such compounds increases the volume, raises the boiling point, and changes the solubilities in approximately the same way. This suggested that the field of force about a group in a molecule is characteristic of that group and, as a first approximation independent of the nature of the rest of the molecule. This concept was named the *principle of independent surface action.*

This principle, which was admittedly a simplification, enabled Langmuir to calculate interactions between groups, and to calculate approximately a number of physical properties of substances, such as mixture energies, and mutual solubilities, with reasonable general agreement with observed values, from the molecular constitution of the substances, *i.e.*, from the number of CH_2, CH_3, OH, Cl, COOH, etc., groups present. The theory was tested by Smyth and Engel.[114] They found that although the assumptions which Langmuir used were too simple to permit general and exact application, nevertheless for less polar substances the approximate agreement between calculated and observed results indicated that the theory bore a useful relation to fact.

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[110] Fink, Dent, and Fink, *Nature,* 160, 801 (1947).

[111] Wm. Stepka and R. Goodwin, *personal communication.*

[112] Langmuir, *J. Am. Chem. Soc.,* 39, 1888 (1917).

[113] Langmuir, *Colloid Symposium Monograph,* 3, 48 (1925).

Martin[115] has shown how, in partition chromatography, the partition coefficient can be related to the molecular structure of a substance by an argument which involves in essence the principle of independent surface action. Since R and R_F can be simply related to the partition coefficient α (see above, Section II), and, allowing the simplifying assumptions inherent in the principle of independent surface action, α can be related to derivable parameters for groups in molecules it theoretically becomes possible to judge separabilities and solvent systems on the basis of this principle. Bate-Smith and co-workers[116] have tested out the application of these ideas to a variety of phenolic substances separable on paper. The results are encouraging but, taken with those of Shibata *et al.*,[117] they suggest caution in the use of the quantitative terms. An interesting regularity has been found by Bate-Smith and Westall.[116] These authors defined a term R_M:

$$R_M = \log [(1/R_F) - 1]$$

R_M is a simple function of temperature and of the relative volumes of solvent phases. For these reasons this term may be somewhat more useful than R_F. This work, like the analogous and independent work of LeRosen (see end of Chapter VIII) is most promising.

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[114] Smyth and Engel, *J. Am. Chem. Soc.*, 51, 2646, 2660 (1929).

[115] Martin, *Biochem. Soc. Symposia*, 3, Cambridge Univ. Press, London, 1949, p. 4.

[116] Bate-Smith and Westall, *Biochim. Biophys. Acta*, 4, 427 (1950); Bradfield and Bate-Smith, *ibid.*, 4, 441 (1950).

[117] Shibata, Takito and Tanaka, *J. Am. Chem. Soc.*, 72, 2789 (1950).

CHAPTER XI

On the Use of Adsorption

I. INTRODUCTION

The first part of the chapter describes short experiments which can be used to familiarize oneself with some of the ways in which adsorption may be utilized. The general ideas and principles of previous chapters may be recalled to explain and rationalize the experiments.

In the second part of this chapter there is suggested a method of solving problems by the use of adsorption.[1]

II. FAMILIARIZING EXPERIMENTS

For these experiments there should be on hand the ordinary solvents and some adsorbents such as a decolorizing charcoal, adsorbent alumina, adsorbent silica gel or silicic acid, U. S. P. precipitated chalk (calcium carbonate), and confectioner's powdered sugar (multiple x). For one of the experiments Florex xxx is needed.

1. Decolorization

As a decolorization experiment one may use one of the tests suggested for evaluating adsorbents[2]: the iodine test, or the methylene blue test. For the iodine test make up a solution in the ratio 2.7 g. iodine plus 4.1 g. potassium iodide in 1 liter of solution. Mix thoroughly and standardize with 0.01 *N* thiosulfate using 25 ml. of solution plus 10 ml. of 5% (by volume) hydrochloric acid. To 0.5 g. charcoal in a 250-ml. Erlenmeyer flask add 10 ml. 5% hydrochloric acid solution, swirl to wet the adsorbent, and bring cautiously to a boil to expel air. Let cool, then add 100 ml. of the iodine solution. Stopper the flask (glass stopper) and shake thirty seconds. Filter immediately allowing all the solution to drain through the filter paper, stir the filtrate, and titrate a 50-ml. aliquot with thiosulfate, using starch solution as an end-point indicator. The extent of decolorization is measured as (g./liter in stock solution) — (g./liter in decolorized solution)/(g./liter in stock solution). The isotherm for iodine can be obtained by treating various dilutions of the stock solution with the same weight of charcoal and plotting weight or moles adsorbed against concentration of the "decolorized" solution. Note that equilibrium may not be reached in this test, and that the iodine removed from solution may not all be adsorbed.

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[1] G. Polya, *How to Solve It.* Princeton Univ. Press, Princeton, 1945.

[2] J. W. Hassler, *Active Carbon, The Modern Purifier.* Industrial Chemical Sales Division, West Virginia Pulp and Paper Company, New York, 1941.

A methylene blue decolorization test with an adsorbent may be carried out as follows. A stock solution containing 1.0 g. methylene blue per liter is made up. To 1 g. of the adsorbent being tested (in a 250 ml. beaker) add the methylene blue solution from a burette, a few ml. at a time, with stirring for 1 min. after each addition. At the end of each stirring period a drop of the mixture is placed on a white spot-plate and examined. A blue color indicates the end-point. The amount of solution used up to this point is a measure of the extent of adsorption. A breakthrough experiment may be run by making a column of the adsorbent in a tube and running the stock solution in until the color breaks through at the bottom. The volume collected to this point is the breakthrough volume.

2. Chromatography

A. COLORED ADSORPTIVES

An experiment very similar to one of those performed by Tswett[3] can be carried out in the following way.[4] A small amount of fresh grass or a carrot leaf is cut up and rubbed up in a mortar with a few milliters of 95% alcohol and about twice as much petroleum ether. The solvent mixture becomes quite green with the leaf pigments. Acetone may be used instead of the alcohol, but one or the other polar solvent is necessary to help extract the pigments. The polar solvent must be completely removed before adsorption. The green solvent mixture is decanted from the vegetable residue into a separatory funnel and washed with water by swirling the mixture (to avoid emulsion). A milky water layer forms and is drawn off. The washing is continued until the water layer remains clear. The washed petroleum ether layer is separated and about 1 ml. is set aside for later use. The green petroleum ether layer is now carefully dried by swirling in a flask with a little anhydrous sodium sulfate. If all the materials are on hand this whole operation, from green grass to dried green extract, should take less than an hour.

While the pigment extract is drying, a column of adsorbent is prepared. The glass tube of a medicine dropper, or a 15-cm. piece of 7-mm. tubing drawn down slightly at one end, is taken, and a small wad of cotton is placed lightly in the constriction. A little calcium carbonate, U. S. P., or confectioner's sugar is put into the tube and gently packed on the cotton with a flat-end glass rod or wooden stick. Adsorbent is added in small portions and gently pressed down until a column 2.5 to 4 cm. long has been formed. Now the dried leaf extract is dripped into the tube and allowed to run evenly into the adsorbent until a green zone 3 to 4 mm. deep is formed, ahead of which colorless solution has run. If the petroleum ether extract was not washed sufficiently or was not dried, the zone does not form and the green solution runs on through the tube. The green zone is developed with a few milliters of solvent. If the adsorbent is calcium carbonate, use benzene as the developer; if sugar, use petroleum ether solution containing $^1/_3$ to $^1/_4$ part of benzene.

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[3] Tswett, *Ber. deut. botan. Ges.*, 24, 316 (1906).

[4] Cassidy, *Sci. Counselor*, 10, 107 (1947); *Proc. Pharm. Manuf. Assoc. Sci. Med. Conf.*, 1949, 19.

The development is fairly rapid. As the developer passes into the adsorbent the green zone spreads and becomes differentiated into an upper thin dark-green zone, a lower blue-green zone; an orange zone below this, and a fast running yellow zone still lower. The upper green zone is chlorophyll *b*, the blue-green zone is chorophyll *a*, the orange zone contains xanthophylls, and the yellow zone carotenes. The zone of carotenes may easily be washed out of the column. The other zones can be recovered by extruding the column, cutting it between the zones, and eluting each in a separate tube or in a test tube with petroleum ether or benzene containing a drop of alcohol. The separation of individual carotenes or xanthophylls requires more subtle chromatography. This experiment can easily be scaled up. The undried petroleum ether extract, set aside above, can be used with a fresh column of adsorbent to see the effect of traces of polar material on the chromatography. Or, a *trace* of alcohol can be added to some of the dry petroleum ether extract and this chromatographed.

Another simple experiment may be used. A column of U. S. P. calcium carbonate is prepared and wetted at the top with a few drops of water. Before the water soaks in, a drop or so of Shaeffer's V-Black Skrip ink is added. As this passes into the adsorbent it forms a good black zone. On development with water a brilliant chromatogram forms: a purple-red zone at the top; a blue-green zone below this; and a narrow yellow zone still lower. Other inks may be examined in this way. Some contain single pigments, others mixtures, depending on the purpose of the ink. If two or more colors of ink are mixed together they can sometimes be separated on the column to give a striking chromatogram. (The formulas of inks are sometimes changed. The ink used in this experiment was purchased in 1947.)

Paper may be used as the adsorbent. A circle of filter paper is placed between two flat pieces of dry glass, such as lantern slide cover glass, so that a segment of the circle projects beyond the glass. This is trimmed off to give a straight edge of filter paper several inches long. This filter-paper sandwich is held vertical, with the trimmed edge at the top and horizontal. A *very small* drop of Shaeffer's V-Black Skrip ink is placed on the trimmed edge, half-way from one end, and allowed to soak into the filter paper. It forms a semicircular black zone. This is now developed by allowing water to dribble into the paper at the center of the zone from a dropper or pipette. A brilliant chromatogram of concentric semicircular zones (often somewhat irregular in outline) develops. The function of the glass is to contain the water and prevent evaporation from the flat surface of the filter paper. Various dyes and dye mixtures can be examined for homogeneity in this way. After development, portions of the zones can be cut out and subjected to spot tests. Sometimes the chromatogram can be developed on blotting paper, or spot-test paper, without a glass cover (see also Figure VIII-13).

B. COLORLESS SUBSTANCES

A number of experiments with sugars and their derivatives are given by Binkley and Wolfrom.[5] One of these[6] is described here. The adsorbent is Florex xxx (see Chapter VII). To a column of adsorbent 6 cm. long in a 0.9-cm. I.D. tube is applied 0.5 ml. of 95% ethanol solution containing 1 mg. sorbitol (from the reduction of glucose) and 0.9 mg. glucose. The chromatogram is developed with 4 ml. 95% ethanol. The column of adsorbent is extruded and streaked with alkaline permanganate (1 g. $NaOH$, 0.1 g. $KMnO_4$, 10 ml. water) using a brush, and making a light, uniform streak. The reagent turns brown where it crosses the zones, and then, more slowly, turns brown over the rest of the streak as it reacts with the residual ethanol. The zones are separated out and the streaked adsorbent shaved off and discarded. The upper zone contains the sorbitol. Each zone can be eluted with water (6 small portions, totaling *ca.* 15 ml.) and the carbohydrate present determined quantitatively if desired. In one experiment[6] the sorbitol zone was eluted and the eluate titrated by periodate oxidation; *found,* 99.7% of the sorbitol. The lower, D-glucose zone by a reducing sugar determination showed 100% of the glucose.

Lew, Wolfrom, and Goepp[6] reported an experiment with lemon juice. The fleshy portion of a lemon was ground with acid-washed sand and centrifuged. 1 ml. of the liquid was treated with 7 ml. absolute ethanol and the mixture centrifuged. 1 ml. of the supernatant was chromatographed on a 0.9 × 6 cm. column of Florex xxx, using 2 ml. 95% ethanol as developer. The column was extruded and examined by the brush method for zones. A streak made with 2,6-dichlorophenolindophenol reagent (5 mg. to 20 ml. water) showed a zone of ascorbic acid in the region 3.9 to 4.3 cm. from the top of the column. A streak with alkaline permanganate showed at least four zones. A streak with Congo red showed the presence of much acid above the ascorbic acid zone.

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[5] W. W. Binkley and M. L. Wolfrom, "Chromatography of Sugars and Related Substances," *Scientific Report Series, No. 10,* Sugar Research Foundation, Inc., New York, 1948.

[6] Lew, Wolfrom, and Goepp, *J. Am. Chem. Soc.,* 68, 1449 (1946).

3. Use of Ion Exchangers

In separate tubes two adsorption columns are prepared. In each case the chromatography tube (0.9 cm. diameter) is closed at the bottom and half-filled with water. Into one tube is sifted a cation exchanger (granular or bead) in the acid form until a column about 4 cm. high is produced. In the other, in a similar manner, a column of acid-adsorbent resin is formed. These columns are washed with distilled water until the effluent is neutral and then kept covered with water. The rate of flow through the columns should be slow, and can be adjusted with a rubber tube and screw clamp on the stem of the column. A dilute solution of sodium acetate (about 1 N) is prepared. This should be basic to test paper. For emphasis a few drops of sodium hydroxide may be added to the solution. 2 or 3 ml. of this basic solution are passed through the acid-form cation exchanger and rinsed in with an equal volume of water. Because of the exchange of H^+ for Na^+ the effluent will be acid. Indicator test paper shows this very clearly: inflowing *basic* solution, outflowing *acid* solution. The acid solution is then put through the acid-adsorbent column. The effluent is *neutral.* Breakthrough experiments can be carried out, using test paper to indicate the end-point, or the experiment may employ the exchange of barium ions from barium chloride, the end-point being found by spot tests with sulfate. A demonstration using the experiment with sodium acetate can be completed in 5 to 10 minutes.

4. Partition Chromatography on a Column

The experiment described here is taken from Ramsey and Patterson.[7] 5 g. of Mallinckrodt AR silicic acid precipitated powder (or other reagent grade of silicic acid) is mixed in a mortar with 1 ml. of bromocresol green indicator solution (100 mg. dyestuff in 25 ml. water + 1.5 ml. *ca.* 0.1N ammonia water). Sufficient 1N ammonia water is mixed in to give the alkaline color of the dyestuff (pale bluish-green); about 0.05 to 0.1 ml. is needed. Water is now mixed in. The exact amount of water has to be determined by trial. For one lot of silicic acid 1.5 ml. sufficed. Into this is mixed a few milliliters of 1% butanol–chloroform solvent to make a slurry, then 25–30 ml. more until the slurry pours readily. (The 1% butanol–chloroform is made by washing U. S. P. chloroform three times with $^1/_2$ volume of water to remove alcohol, adding to 1 liter of washed chloroform 10 ml. acid-free butanol with vigorous shaking, then 25 ml. water. The thoroughly shaken mixture is allowed to stand until clear; the choroform solution equilibrated in this way with water is drawn off and the excess water is discarded.) A wad of cotton is placed in an 0.9 cm. I.D. × *ca.* 30 cm. chromatogram tube and the slurry poured in. Slight pressure is used to force the excess solvent dropwise from the column. When the suspension becomes so viscous that it will not pour when the tube is tilted, the column is ready for use. It should not be allowed to dry below the surface of the gel. A mixture of acetic, propionic, and butyric acids is now applied to the column by carefully running in 0.5 ml. of 0.1 *N* soutions of each in 1% butanol–chloroform. When the last portion of solution has run into the gel rinse in with a little more solvent, then fill the tube with solvent, apply slight pressure, and observe the development. When the lowest zone (butyric acid) migrates out of the column, change the developer to 10% butanol–chloroform. This speeds up the movement of the propionic (lower) and acetic (upper) zones. (The 10% butanol–chloroform is made by mixing 900 ml. U. S. P. chloroform with 100 ml. *n*-butanol and equilibrating with 25 ml. of water. The chloroform is not washed first.) A good column will separate the acids into three well-differentiated yellow zones, each of which can be collected separately as the acid passes out of the column.

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[7] Ramsey and Patterson, *J. Assoc. Offic. Agri. Chem.*, 28, 644 (1945).

5. Partition Chromatography on Paper

For this experiment there are needed sheets of filter paper about 18 × 22.5 in., though small pieces may be used, see below; a solution made by mixing reagent grade phenol (75 g.) with distilled water (25 g.), and 0.01 *M* solutions of several amino acids in 75% alcohol, or a small amount of a protein hydrolyzate which has been repeatedly boiled down with water *in vacuo* to a small volume to remove hydrochloric acid. There are also needed a glass cylinder of suitable size such as a 1000-ml. cylinder, a 0.1% solution of ninhydrin in *n*-butanol, and an atomizer.[8]

A piece of filter paper is cut to such a size that when bent around into a cylinder it will stand up in the available glass cylinder without touching the sides or reaching quite to the top.[9] About one inch from what will be the lower edge of this paper cylinder a line is drawn parallel to the edge. *Very small* drops of amino acids are placed at about 0.75–1-in. intervals along this line starting about 1–1.5 in. from the margin. Amino acid spots can be superimposed provided each is allowed to dry before the next is applied. The usual difficulty encountered in beginning this kind of work is that too much amino acid is put on the paper. The paper must not be touched with the hands. The extra folds for stiffening shown in Figure X-4 are not necessary when the diameter of the paper cylinder is small.

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[8] Consden, Gordon, and Martin, *Biochem. J.*, 38, 224 (1944).

[9] Williams and Kirby, *Science*, 107, 481 (1948).

After the spots have dried, the paper is formed into a cylinder and the edges are stapled together without quite touching. This cylinder is then stood in the glass cylinder in 1.25 to 0.5 in. of phenol solution. The glass cylinder is then sealed shut with a glass or metal plate and tape. The phenol will rise some 24 cm. in about as many hours. When the front of the developer—the line demarking the obviously damp from the dry part—has risen to near the top of the paper it is taken from the cylinder, opened out, and air-dried. A fan may be used. The paper is then sprayed lightly with ninhydrin solution, allowed to dry, and then hung in an oven at about 75° until the ninhydrin color develops. (The ninhydrin color will develop in 24 hrs., at room temperature, and is then more stable.[10]) In a good experiment the amino acids will form round or oval spots lined up above the original spot (though glutamic and aspartic acids have a tendency to "streak"). Improved spreading out of the spots can be obtained by running a two-dimensional chromatogram as described in Chapter X.

The paper strip method can be run more quickly, as Rockland and Dunn have shown.[11] A 6-in. test tube with a well-fitting cork serves as the chamber (Fig. X-5). A strip of filter paper 13.5 cm. long, 1.0 cm. wide at the bottom edge, and 1.8 at the top is used. In the middle near the top of the paper a small hole is made. A tiny drop of amino acid solution or mixture is placed about 6 mm. from the narrow end of the paper by touching it lightly with a capillary pipette containing the solution. The wet spot should not be over 1.5 mm. in diameter. It is circled lightly in pencil and let dry. About 0.4 ml. of phenol–water solution is placed in the test tube and the filter paper put in as shown in Figure X-5. The upper, wider end of the filter paper should just fit in the diameter of the tube and so prevent the rest of the paper from touching the sides. The tube is stoppered and let stand 2–3 hrs. The rest of the procedure is as described above. Rockland and Dunn use a small hook to manipulate the strip, and spray with 0.25% ninhydrin solution in water-saturated butanol. The reasoning on which this quicker method is based is that, since the objective of the method is to obtain well-separated spots with clear filter paper in between, then if one uses large spots, say 1 cm. in diameter, the development must continue at least until the solvent front has moved more than 1 × (the number of amino acids) cm. With very small spots the distance the front must move is correspondingly decreased. The time required to resolve the very small spots is actually decreased on two counts: the shorter path which is needed and the additional fact that the front moves fastest at first and then gradually slows down with distance traveled.

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[10] Dent, *Biochem. J.*, **43**, 169 (1948).

[11] Rockland and Dunn, *Science*, **109**, 539 (1949).

III. SOLUTION OF PROBLEMS OF SEPARATION

If a mixture is to be separated, and there is no information in the literature on already accomplished separation of mixtures like or analogous to this, then certain steps may be taken to simplify the problem of the separation. The mixture is first classified as being amenable to one of the separation procedures of Chapters VII–X, and then is treated in some such way as follows.

The components of the mixture may be recognizable by special tests. This would greatly facilitate the separation. But it will be assumed here that they are colorless and not specifically recognizable, thus taking the most general and difficult case. A part of the original mixture is made up into a solution of known concentration with some appropriate solvent—neither a very poor nor a very good solvent. It is then tested for adsorption against several adsorbents either by treating with weighed amounts of adsorbent and determining the extent of adsorption by evaporating solvent from an aliquot of the equilibrium solution, or by determining the breakthrough or threshold volume for small columns of the adsorbents as in the experiments given above; or by one of the "partition" methods if the mixture is of a kind classified to be amenable to this method of separation. The object here is to obtain enough information about the mixture to enable a choice of solvent and adsorbent, and an approximate determination of the amount of adsorbent which will be needed. The former may be facilitated by obtaining for each adsorbent two points on an isotherm for the mixture, possibly also from more than one solvent. An inspection of the slopes of the lines through each pair of points gives an estimate of the strength of the adsorbent (see Fig. IV-1). The second objective can be approached by calculating approximately the equilibrium adsorption at the concentration of the original solution (as from a breakthrough experiment) and from this the amount of adsorbent which would just hold a given amount of mixture in a single zone. This is multiplied by 3 or 5 (etc.) to allow for the development of the chromatogram and the total weight of the adsorbent is mixed with enough filter-aid to give a flow velocity of, say, 5 to 15 mm. per minute when packed in a tube to produce a column about 5 to 10 times as high as it is wide.

After the column of adsorbent has been prepared the mixture is applied to it and developed with more solvent or another solvent, or a graded series of solvents, as illustrated in Table V-4. Development is continued until material appears at the foot of the column, whereupon two courses are open. Either the development is continued, and portions of percolate are collected and analyzed, so that a concentration profile of the percolate can be plotted (as in Figure X-1, for example) or the development is stopped, the column extruded, sectioned, and the sections eluted, so that a concentration profile of the column itself can be plotted. In either case the zones are recognizable from the profiles as described in previous chapters.

It can often be judged from the shapes of the zone profiles whether a clean-cut separation has been made. Thus zones separated by pure solvent or by empty adsorbent would be likely to be discrete substances. Rechromatography of the contents of a zone, preferably with a different solvent–adsorbent pair would constitute a further test of homogeneity of a fraction. Rechromatography with the same solvent–adsorbent pair would indicate whether destruction or alteration on the adsorbent were occurring.

In general, in attacking a problem such as this the differential countercurrent methods would be the methods of choice unless the problem were a very simple one or was of the special kind referred to in Chapter IX, section VII. As was pointed out above, even a simple decolorization may be performed rapidly and efficiently with a column of adsorbent.

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